

ERRATA

Page

- 11 10th line from bottom change 4.167 to 4.115.
56 Line 16, parenthesis on numerator before "X 100."
60 1st line, change "distillate" to "residue."
61 1st line, change "distillate" to "residue."
121 Lines 4 and 5 from bottom, change 35.5 to 36.5.
144 Line 6 from bottom, change 0.0623 to 0.0618.
144 Line 8 from bottom, change 0.0089 to 0.00883.
145 Line 8 from bottom, change 0.0089 to 0.00883.
145 Line 8 from bottom, change 0.356 to 0.530.
145 Line 5 from bottom, change 0.356 to 0.530.
145 Line 5 from bottom, change 0.367 to 0.547.
147 Line 4 change 0.0243 to 0.243.
147 Line 8 change 0.0243 to 0.243.

A LABORATORY MANUAL FOR
THE CHEMICAL ANALYSIS OF
WATER AND SEWAGE

FIRST EDITION

By

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PREFACE

The authors have long felt the need for a simple and concise laboratory manual of water and sewage chemical analysis and have sought to fill that need in the preparation of this book.

The book contains specific directions in outline form for making the chemical determinations necessary for the control of water and sewage treatment plants, the analysis of polluted water, and the examination of industrial wastes. Each determination is accompanied by calculation formulae, many of which are numerically illustrated. In addition to the specific directions for the tests, the book contains methods of sampling, laboratory technique, a discussion of the chemistry involved, interpretation of results, and related topics, making it more valuable as a general manual for those using the results of water and sewage analysis.

The manual will be useful to:

(1) Those engaged in water and sewage treatment plant operation who find it necessary, along with other duties, to make certain laboratory determinations, but because of lack of training in chemistry must rely upon specific directions in carrying out the steps involved.

(2) Those with some training in chemistry, but having only infrequent occasion to make certain laboratory determinations on water, sewage and industrial wastes.

(3) The plant chemists who will find the manual a convenient and ready reference.

(4) The sanitary engineer engaged in making stream surveys or studying the characteristics of water or sewage in connection with plant design.

(5) Colleges and universities offering instruction in water and sewage analysis who will find the manual useful as a laboratory guide.

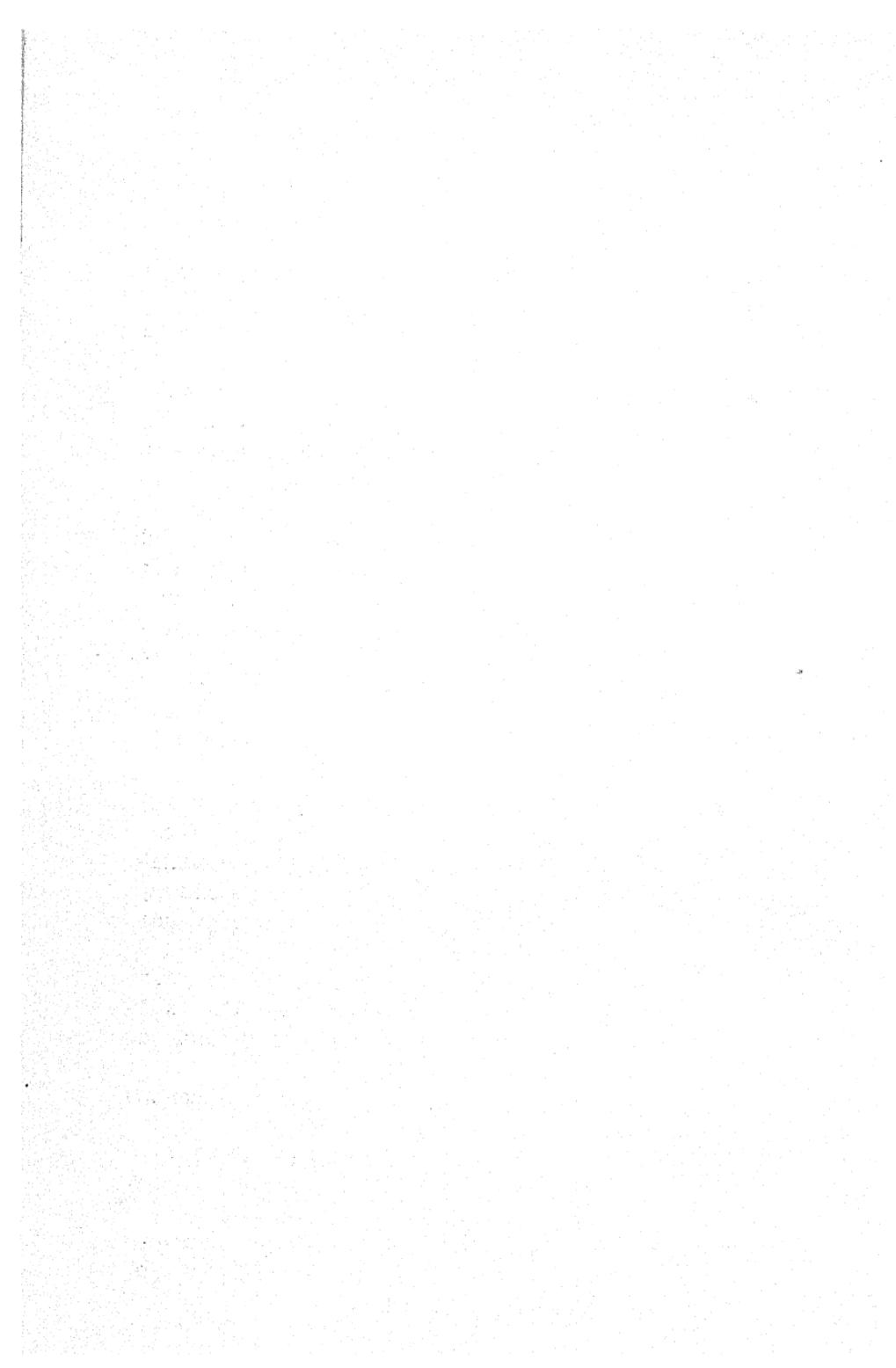


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SECTION I

METHODS OF ANALYSIS

Part A. Water Analysis

Note. Numbers inclosed in parentheses, thus (3), refer to numbered reagents and solutions in Section II.

Total Solids

1. Clean a platinum evaporating dish and place it in a 103°C oven for one hour, or if the loss on ignition determination is also to be made, ignite to low red heat in the muffle furnace or over a burner. (A platinum dish is to be preferred but others may be used.)
2. Place the dish in a desiccator to cool, and weigh.
3. Place the weighed dish on a steam or water bath.
4. Thoroughly mix the sample and measure out 100 ml. (a larger volume may be used) by means of a volumetric flask.
5. Transfer the sample to the dish, rinse the flask several times with small portions of distilled water, and add the rinsings to the dish, being sure that all suspended matter is transferred.
6. After the sample is evaporated, dry the dish and residue in the 103°C oven for one hour, cool in the desiccator and weigh.

Calculations

$$\frac{\text{Increase in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m.}$$

total solids.

Example

Sample	No. 1	No. 2
Wt. of dish and residue due (100 ml.)	48.2982 gms.	43.8646 gms.
Wt. of dish	48.2540 "	43.8210 "
Wt. of residue	0.0442 "	0.0436 "
Total solids No. 1	$\frac{0.0442 \times 1,000,000}{100} = 442$ p.p.m.	

$$\text{Total solids No. 2 } \frac{0.0436 \times 1,000,000}{100} = 436 \text{ p.p.m.}$$

$$\text{Average} = 439 \text{ p.p.m.}$$

Loss on ignition

1. Place the evaporating dish and residue from the total solids determination in the muffle furnace, or ignite over a burner, at low red heat until the ash is white or nearly so.
2. Allow the dish to cool and moisten the residue with a few drops of distilled water.
3. Dry in the 103°C oven for one hour, cool in a desiccator and weigh.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m. loss}$$

on ignition.

Example

Sample	No. 1	No. 2
Wt. of dish and residue due (100 ml.)	48.2982 gms.	43.8646 gms.
Wt. of dish and ash	48.2891 "	43.8551 "
Loss in weight	0.0091 "	0.0095 "
Loss on ignition No. 1	$\frac{0.0091 \times 1,000,000}{100} = 91$ p.p.m.	

$$\text{Loss on ignition No. 2 } \frac{0.0095 \times 1,000,000}{100} = 95 \text{ p.p.m.}$$

$$\text{Average} = 93 \text{ p.p.m.}$$

Suspended and dissolved solids, Gooch crucible method
 Reagents. Section II, No. (1)

1. Pour about 25 ml. of a thin emulsion of asbestos fiber (1) into a Gooch crucible.
2. Apply the suction gently until the mat is formed.
3. Wash with distilled water until no fibers of asbestos run through the filter.
4. Dry the crucible and ignite at a low red heat. Cool, moisten with distilled water, dry at 103°C for one hour, cool in a desiccator and weigh. (Igniting and moistening may be omitted if the loss on ignition of suspended solids is not to be determined.)
5. Measure 100 ml. (use a larger sample if the suspended matter is low) of the well mixed water by means of a volumetric flask.
6. Filter the sample through the prepared Gooch crucible and also several distilled water rinsings of the flask being sure that all suspended matter has been transferred to the crucible.
7. Dry in the oven at 103°C , cool in the desiccator and weigh.

Calculations

$$\frac{\text{Increase in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m.}$$

suspended solids.

$$\begin{aligned} \text{P.p.m. total solids} - \text{p.p.m. suspended solids} \\ = \text{p.p.m. dissolved solids.} \end{aligned}$$

Example

Sample	No. 1	No. 2
Wt. of crucible and solids (500 ml.)	15.6208 gms.	14.0921 gms.
Wt. of crucible	<u>15.5726</u> "	<u>14.0420</u> "
Wt. of solids	0.0482 "	0.0501 "

$$\begin{aligned} \text{Suspended solids No. 1} & \frac{0.0482 \times 1,000,000}{500} = 96.4 \\ & \text{p.p.m.} \end{aligned}$$

$$\begin{aligned} \text{Suspended solids No. 2} & \frac{0.0501 \times 1,000,000}{500} = 100.2 \\ & \text{p.p.m.} \end{aligned}$$

$$\text{Average} = 98.3 \text{ p.p.m.}$$

$$\text{Dissolved solids} = 439 - 98.3 = 340.7 \text{ p.p.m.}$$

Loss on ignition, suspended and dissolved solids,
Gooch crucible method

1. Ignite the crucible from the suspended solids determination at low red heat.
2. Cool and moisten the ash with a few drops of distilled water.
3. Dry in the oven at 103°C for one hour, cool in the desiccator and weigh.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m. loss}$$

on ignition of suspended solids.

$$\text{P.p.m. loss on ignition total solids} - \text{p.p.m. loss on ignition of suspended solids} = \text{p.p.m. loss on ignition dissolved solids.}$$

Example

Sample	No. 1	No. 2
Wt. of crucible and solids (500 ml.)	15.6208 gms.	14.0921 gms.
Wt. of crucible and ash	15.6000 "	14.0711 "
Loss in weight	0.0208 "	0.0210 "

$$\text{Loss on ignition No. 1 } \frac{0.0208 \times 1,000,000}{500} = 41.6 \text{ p.p.m.}$$

$$\text{Loss on ignition No. 2 } \frac{0.0210 \times 1,000,000}{500} = 42.0 \text{ p.p.m.}$$

$$\text{Average} = 41.8 \text{ p.p.m.}$$

$$\text{Loss on ignition dissolved solids} = 93 - 41.8 \\ = 51.2 \text{ p.p.m.}$$

Dissolved and suspended solids, filtration method

1. Filter a portion of the water sample through a filter paper.
2. Repeat the method given for the total solids determination using 100 ml. of the above filtrate.

Calculations

$$\frac{\text{Increase in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m.}$$

dissolved solids.

$$\begin{aligned} \text{P.p.m. total solids} - \text{p.p.m. dissolved solids} \\ = \text{p.p.m. suspended solids.} \end{aligned}$$

Example

Sample	No. 1	No. 2
Wt. of dish and resi-		
due (100 ml.)	48.2882 gms.	43.8546 gms.
Wt. of dish	48.2540 "	43.8210 "
Wt. of dissolved solids	0.0342 "	0.0336 "

$$\text{Dissolved solids No. 1 } \frac{0.0342 \times 1,000,000}{100} = 342 \text{ p.p.m.}$$

$$\text{Dissolved solids No. 2 } \frac{0.0336 \times 1,000,000}{100} = 336 \text{ p.p.m.}$$

$$\text{Average} = 339 \text{ p.p.m.}$$

$$\text{Suspended solids} = 439 - 339 = 100 \text{ p.p.m.}$$

Loss on ignition, dissolved and suspended solids, filtration method

1. Ignite the dish from the dissolved solids determination at low red heat.
2. Cool and moisten the residue with a few drops of distilled water.
3. Dry in the oven at 103°C for one hour, cool in the desiccator and weigh.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m. loss}$$

on ignition of dissolved solids.

$$\begin{aligned} \text{P.p.m. loss on ignition total solids} - \text{p.p.m. loss} \\ \text{on ignition dissolved solids} = \text{p.p.m. loss on ignition suspended solids.} \end{aligned}$$

Example

Sample	No. 1	No. 2
Wt. of dish and resi- due (100 ml.)	48.2882 gms.	43.8546 gms.
Wt. of dish and ash	<u>48.2832</u> "	<u>43.8493</u> "
Loss in weight	0.0050 "	0.0053 "
Loss on ignition dissolved solids No. 1		
	$\frac{0.0050 \times 1,000,000}{100} = 50 \text{ p.p.m.}$	

Loss on ignition dissolved solids No. 2

$$\frac{0.0053 \times 1,000,000}{100} = 53 \text{ p.p.m.}$$

$$\text{Average} = 51.5 \text{ p.p.m.}$$

$$\begin{aligned} \text{Loss on ignition suspended solids} &= 93 - 51.5 \\ &= 41.5 \text{ p.p.m.} \end{aligned}$$

Alkalinity

Reagents. Section II, Nos. (2), (3), (4).

1. Pipette 100 ml. of the sample into one Erlenmeyer flask and the same quantity of distilled water into another.
2. Add four drops of phenolphthalein indicator (2) to each.
3. If the sample becomes pink, add 0.02 N sulphuric acid (3) from a burette until the pink color just disappears and record the number of ml. of acid used.
4. Add two drops of methyl orange indicator (4) to each flask.
5. If the sample becomes yellow, add 0.02 N sulphuric acid until the first difference in color is noted when compared with the distilled water. The end point is orange. (Methyl orange is yellow in alkaline solution, orange in neutral, and red in acid.) Record the number of ml. of acid used.

Calculations

Total alkalinity as p.p.m. CaCO_3 = total ml. acid $\times 10$.

Differentiation of alkalinites due to OH , CO_3 and HCO_3 .

Let P = the ml. of 0.02 N sulphuric acid used for the titration with phenolphthalein and T = the ml. of the acid used for the total titration (phenolphthalein plus methyl orange).

There are five possible conditions as follows:

1. $P = T$

$$\text{Hydroxide (p.p.m.)} = P \times 10$$

2. P greater than $1/2 T$

$$\text{Hydroxide (p.p.m.)} = (2P - T) \times 10$$

$$\text{Normal carbonate (p.p.m.)} = 2(T - P) \times 10$$

3. $P = 1/2 T$

$$\text{Normal carbonate (p.p.m.)} = T \times 10$$

4. P less than $1/2 T$

$$\text{Normal carbonate (p.p.m.)} = 2P \times 10$$

$$\text{Bicarbonate (p.p.m.)} = (T - 2P) \times 10$$

5. $P = 0$

$$\text{Bicarbonate (p.p.m.)} = T \times 10$$

All of the above results are in terms of p.p.m. as CaCO_3 .

Examples

The five possible alkalinity conditions are illustrated in the five different results of the titrations given in the following table.

Condition	Volume of sample, 100 ml.			Alkalinites (p.p.m. as CaCO_3)		
	Results of titration		$\text{ml. of 0.02 N acid}$	Hydroxide	Carbonate	Bicarbonate
	P	T		(OH)	(CO_3)	(HCO_3)
1	18	18	180	0	0	0
2	12	18	60	120	0	0
3	9	18	0	180	0	0
4	6	18	0	120	60	0
5	0	18	0	0	0	180

Acidity

Reagents. Section II, Nos. (2), (5).

1. Pipette 110 ml. of the sample into one Erlenmeyer flask and the same quantity of distilled water into another.
2. Add 4 drops of phenolphthalein indicator (2) to each.
3. Add 0.02 N sodium hydroxide (5) from a burette to the sample until the first permanent pink color appears and record the number of ml. of sodium hydroxide used.

Calculations

Ml. of 0.02 N NaOH X 10 = p.p.m. total acidity expressed in terms of CaCO₃.

Carbon dioxide (CO₂)

Reagents. Section II, Nos. (2), (6).

1. Fill a 100 ml. Nessler tube to the mark with the freshly taken sample.
2. Add 10 drops of phenolphthalein indicator (2).
3. Titrate rapidly with N/44 sodium hydroxide (6) from a burette, stirring gently, until a slight permanent pink color appears. Record the number of ml. of sodium hydroxide used.

Calculations

Ml. of N/44 NaOH X 10 = p.p.m. carbon dioxide.

Note

This test should be made at the time the sample is taken because of the ease with which the carbon dioxide escapes. If this is not possible, the sample bottle should be completely filled and stoppered and the sample kept at a temperature lower than that at the time it was collected.

Hydrogen-ion concentration (pH)

There are two general types of apparatus adapted for the determination of hydrogen-ion concentration, the colorimetric and electrometric. Each of these are best adapted to special conditions. The colorimetric type is best suited for the usual conditions found in determining the pH of water.

There are many kinds of colorimetric pH outfits on the market most of which are of equal accuracy and convenience for water analysis determinations. There are two general types (a) those having color disks and (b) those having standard color solutions.

The following general method can be applied to almost all of the colorimetric outfits.

1. Place 10 ml. of the sample into each of the two or three tubes provided.
2. To one tube add the designated quantity of indicator solution. (The other tubes do not receive the indicator.)
3. Place the tubes in the comparator in such a manner that the color standards are opposite the tubes not containing the indicator. The color comparison must be made by looking through the same thickness of liquid having the same color and turbidity as the sample.
4. Compare the colors, select and read the pH of the tube having a color nearest that of the sample.

Total hardness, soap method

Reagents. Section II, No. (7).

1. Pipette 50 ml. of distilled water into a glass-stoppered 8-ounce bottle.
2. Add standard soap solution (7) a drop at a time from a burette, shaking the mixture vigorously after each addition.
3. The end-point is reached when a permanent lather is produced which will remain as a complete cover over the surface of the water for 5 minutes with the bottle lying on its side.
4. Record the ml. of soap solution used. This is called the "lather factor."
5. Pipette 50 ml. of the sample into a similar bottle.
6. Add the soap solution in small portions at first (0.5 ml.), shaking vigorously after each addition.
7. As the end-point is approached, the quantity added should be reduced to 0.1 ml. for each addition.

8. After a permanent lather is produced which will last for 5 minutes with the bottle on its side, record the ml. of soap solution used.
9. Continue the addition of small quantities of soap solution. If the lather again disappears, the first end-point was false due to the presence of magnesium salts.
10. Continue the addition of the soap solution until the true end-point is reached.
11. If the quantity of soap solution used is greater than 7 ml., repeat the procedure (No. 5 to 10) using a smaller sample diluted to 50 ml. with distilled water.

Calculations

$$\frac{(\text{ml. soap solution} - \text{ml. lather factor}) \times 1000}{\text{ml. of sample}}$$

= p.p.m. total hardness expressed as CaCO_3 .

Example

ml. of sample used	50.0
ml. of soap solution for lather factor	0.4
ml. of soap solution for sample	6.2

$$\frac{(6.2 - 0.4) \times 1000}{50} = 116 \text{ p.p.m. total hardness}$$

as CaCO_3 .

Total hardness, soda-reagent method

Reagents. Section II, Nos. (4), (3), (8).

1. Pipette 200 ml. of the sample into a 500 ml. Erlenmeyer flask.
2. Add four drops of methyl orange (4).
3. Add 0.02 N sulphuric acid (3) from a burette until the first permanent color change is observed.
4. Place 200 ml. of distilled water into a second flask.
5. Boil each for 5 minutes.
6. Add exactly 25 ml. of soda-reagent (8) to each flask and boil for 10 minutes and until the volume is reduced to about 150 ml.

7. Cool and pour into a 200 ml. volumetric flask, rinsing the solutions into the flasks with small quantities of boiling distilled water.
8. Make up to the mark with boiled distilled water and mix.
9. Filter each solution, rejecting the first 50 ml. of each filtrate.
10. Pipette a 50 ml. portion of each filtrate into an Erlenmeyer flask, add 4 drops of methyl orange, and titrate each portion with 0.02 N sulphuric acid, recording the ml. of acid used.

Calculations

(ml. 0.02 N H_2SO_4 used for distilled water - ml. of 0.02 N H_2SO_4 used for sample in Step No. 10)
 $X 20 = \text{p.p.m. total hardness as } \text{CaCO}_3$.

Example

Ml. of 0.02 N H_2SO_4 used for distilled water	31.2
Ml. of 0.02 N H_2SO_4 used for sample in Step 10	<u>19.6</u>
Difference	<u>11.6</u>

$$11.6 X 20 = 232 \text{ p.p.m. total hardness as } \text{CaCO}_3$$

Total hardness, gravimetric method

Use the gravimetric methods for the determination of calcium and magnesium (iron and aluminum if present in large amounts) given on pages 16 to 18.

Calculations

$$(\text{p.p.m. Ca} X 2.496) + (\text{p.p.m. Mg} X 4.167) = \text{p.p.m. total hardness as } \text{CaCO}_3$$

Note

If iron and aluminum are present in any considerable quantity, they must be determined and the values changed to terms of CaCO_3 . These results must then be added to the hardness as determined above. To change Fe_2O_3 to CaCO_3 multiply by 1.872. To change Al_2O_3 to CaCO_3 multiply by 2.932.

Carbonate and non-carbonate hardness

The carbonate and non-carbonate hardness may be calculated from the results of the alkalinity and total hardness determinations.

Calculations

Carbonate hardness.

Let p.p.m. normal carbonate alkalinity + p.p.m. bicarbonate alkalinity = S.

Case I. Where S is equal to or less than the total hardness, then S = carbonate hardness.

Case II. Where S is greater than the total hardness then the total hardness = the carbonate hardness.

Non-carbonate hardness.

P.p.m. total hardness - p.p.m. carbonate hardness
= p.p.m. non-carbonate hardness.

Magnesium, volumetric method

Reagents. Section II, Nos. (2), (3), and (9).

1. Pipette 100 ml. of the sample into a 250 ml. Erlenmeyer flask.
2. Add just sufficient 0.02 N sulphuric acid (3) to neutralize the total alkalinity. (Use the quantity of acid as determined on a separate portion of sample.)
3. Boil down to about one-half the volume.
4. Rinse into a 200 ml. volumetric flask using small portions of freshly boiled, hot, distilled water.
5. Place 100 ml. of freshly boiled, hot, distilled water in a second 200 ml. volumetric flask.
6. Add exactly 25 ml. of a clear solution of saturated limewater (9) to each flask.
7. Fill each to the mark with boiled, hot, distilled water.
8. Stopper loosely with a rubber stopper and after mixing well, set on the steam bath for 1 hour.
9. Remove the flasks from the bath and quickly filter a portion through a filter paper.

10. Immediately pipette 50 ml. of the filtrate from each flask into Erlenmeyer flasks and titrate with 0.02 N sulphuric acid (3) from a burette after adding a few drops of phenolphthalein indicator (2).

Calculations

(ml. of 0.02 N H_2SO_4 for distilled water - ml. of 0.02 N H_2SO_4 for sample) X 9.72 = p.p.m. magnesium as Mg.

Sulphate, volumetric method

Reagents. Section II, Nos. (2), (10), (11), (12).

1. Measure exactly 250 ml. of the sample into a 400 ml. beaker.
2. Add 10 ml. of a 1 per cent solution of hydroxyl amine hydrochloride (10). (If the iron content of the sample has previously been shown to be less than 0.5 p.p.m., this step may be omitted.)
3. Add 20 ml. of benzidine hydrochloride (11).
4. Stir vigorously and allow the precipitate to settle.
5. Filter the solution through paper and wash the beaker and paper with small amounts of cold distilled water.
6. Transfer the precipitate from the paper to the original beaker, add 200 ml. of water and heat to boiling to dissolve.
7. Add a few drops of phenolphthalein (2) and titrate with 0.05 N sodium hydroxide solution (12) until the first permanent pink color is obtained.
8. Place the filter paper in the solution and continue the titration to the first permanent pink color. Record the ml. of sodium hydroxide used.

Calculations

ml. of 0.05 N NaOH used X 9.6 = p.p.m. sulphate (SO_4).

Chloride, volumetric method

Reagents. Section II, Nos. (2), (3), (4), (13), (14), (15).

1. Pipette 50 ml. of the sample into a porcelain evaporating dish.
2. Place about the same quantity of distilled water into a second dish for a color comparison.
3. Add 1 ml. of potassium chromate indicator (13) to each.
4. Add standard silver nitrate solution (14) to the sample from a burette, a few drops at a time, with constant stirring until the first permanent reddish coloration appears. This can be determined by comparison with the distilled water blank.
5. If more than 7 or 8 ml. of silver nitrate solution are required, the entire procedure should be repeated using a smaller sample diluted to 50 ml. with distilled water. Record the ml. of silver nitrate used.

Calculations

$$\frac{(\text{ml. of } \text{AgNO}_3 \text{ used} - 0.2) \times 500}{\text{ml. of sample}} = \text{p.p.m. chloride (Cl).}$$

Precautions

If the water sample is highly colored it should be decolorized by shaking with washed aluminum hydroxide (15) and filtering.

If it is acid, add sodium carbonate until it is slightly alkaline to methyl orange (4).

If it is alkaline, add standard sulphuric acid (3) until it is just acid to phenolphthalein (2).

Silica, gravimetric method

1. Evaporate, in an evaporating dish, 250 ml. of well mixed sample, to which a few drops of concentrated hydrochloric acid have been added, to dryness on the water bath.
2. Moisten the residue with a few drops of concentrated hydrochloric acid.
3. Add about 30 ml. of distilled water and heat to boiling. (More water is sometimes required to dissolve calcium sulphate.)

4. Filter through a quantitative filter paper, rinse the dish and wash the residue with distilled water, adding the filtered rinsings and washings to the filtrate. All of the insoluble residue in the evaporating dish must be transferred to the filter paper. (The filtrate may be saved for the iron and aluminum determination.)
5. Fold the paper, place it in a crucible and ignite in the muffle furnace or over a burner.
6. Cool in a desiccator and weigh.
7. Add a few drops of sulphuric acid and a few ml. of hydrofluoric acid to the ash in the crucible.
8. Volatilize the acids by heating gently over a burner.
9. Ignite the crucible, cool in a desiccator and weigh.

Calculations

Loss in weight (grams) X 4000 = p.p.m. silica (SiO_2).

Iron and aluminum oxides, gravimetric method

Reagents. Section II, Nos. (16), (17).

1. Evaporate, in an evaporating dish, 250 ml. of the well mixed sample, to which a few drops of concentrated hydrochloric acid have been added, to dryness on a water bath.
2. Moisten the residue with a few drops of concentrated hydrochloric acid.
3. Add about 30 ml. of distilled water and heat to boiling. (More water is sometimes required to dissolve the calcium sulphate.)
4. Filter, rinse the dish and wash the residue on the paper with distilled water, adding the filtered rinsings and washings to the filtrate. (The above steps are omitted if the filtrate from the silica determination is used.)
5. Add a few drops of bromine water (16) to the filtrate and boil for 5 minutes.
6. Add 10 ml. of 10 per cent solution of ammonium chloride (17), make alkaline to litmus with

- concentrated ammonium hydroxide and boil again for a few minutes.
7. Filter the precipitated iron and aluminum oxides and rinsings of the container onto a quantitative filter paper and wash the filter paper with several small quantities of distilled water, adding the washings to the filtrate. (The filtrate may be saved for the determination of calcium.)
 8. Ignite a crucible, cool in a desiccator and weigh.
 9. Fold the filter paper, place it in the crucible and ignite in the furnace or over a burner.
 10. Cool in a desiccator and weigh.

Calculations

Difference in weight (grams) X 4000 = p.p.m. combined iron and aluminum oxides (Fe_2O_3 and Al_2O_3).

Note

To separate the two oxides, make a determination for total iron according to the method given on page 25. The difference between the combined oxides and the calculated iron oxide (Fe_2O_3) is the aluminum oxide (Al_2O_3).

$$\begin{aligned} & (\text{p.p.m. Fe as determined on page 25}) \times 2.8483 \\ & = \text{p.p.m. } \text{Fe}_2\text{O}_3. \end{aligned}$$

Calcium, gravimetric method

Reagents. Section II, Nos. (16), (17), (18), (19), (20).

1. Evaporate to dryness, in an evaporating dish on a water bath, 250 ml. of the well mixed sample to which a few drops of concentrated hydrochloric acid have been added.
2. Moisten the residue with a few drops of concentrated hydrochloric acid.
3. Add 30 ml. of distilled water and heat to boiling. (More water is sometimes required to dissolve the calcium sulphate.)
4. Filter, rinse the dish and wash the residue on the paper with distilled water, adding the filtered rinsings and washings to the filtrate, but keeping the volume small.

5. Add a few drops of bromine water (16) to the filtrate and boil gently for 5 minutes.
6. Add 10 ml. of a 10 per cent solution of ammonium chloride (17), make alkaline to litmus with concentrated ammonium hydroxide and boil gently for a few minutes.
7. Filter, rinse the beaker and wash the precipitate on the paper with small portions of distilled water, adding the filtered rinsings and washings to the filtrate. (The above steps are omitted if the filtrate from the iron and aluminum determination is used.)
8. Warm the filtrate and add slowly, with constant stirring, 10 ml. of saturated ammonium oxalate (18).
9. Allow to stand for 30 minutes in a warm place.
10. Filter through a quantitative filter paper, rinsing the beaker and paper with small portions of hot distilled water. (The filtrate may be saved for the magnesium determination.)
11. Place the original beaker from which the filtration was made under the stem of the funnel, pierce a hole in the filter paper in the funnel and wash the precipitate into the beaker, with 30 ml. of 2 per cent sulphuric acid (19).
12. Heat to boiling and add from a burette a standard solution of potassium permanganate (20) until the first permanent pink color is obtained.
13. Transfer the filter paper to the beaker and continue the titration with potassium permanganate to the first permanent pink color. Record the total ml. of permanganate used.

Calculations

$$\text{Ml. of } \text{KMnO}_4 \times 10 = \text{p.p.m. calcium (Ca).}$$

Magnesium, gravimetric method

Reagents. Section II, Nos. (16), (17), (18), (21).

1. Evaporate to dryness, in an evaporating dish over a water bath, 250 ml. of the well mixed sample to which a few drops of concentrated hydrochloric acid have been added.

2. Moisten the residue with a few drops of concentrated hydrochloric acid.
3. Add 30 ml. of distilled water and heat to boiling. (Sometimes a larger quantity of water is required to dissolve the calcium sulphate.)
4. Filter, rinse the dish and wash the residue on the paper with small portions of water adding the filtered rinsings and washings to the filtrate.
5. Add a few drops of bromine water (16) and boil for 5 minutes.
6. Add 10 ml. of 10 per cent solution of ammonium chloride (17), make alkaline to litmus with concentrated ammonium hydroxide and boil gently for a few minutes.
7. Filter, rinse the beaker and wash the residue on the paper with small portions of distilled water, adding the filtered rinsings and washings to the filtrate.
8. Warm the filtrate and add slowly, with constant stirring, 10 ml. of a saturated solution of ammonium oxalate (18).
9. Allow the solution to stand for 30 minutes in a warm place.
10. Filter, rinse the beaker and wash the filter paper, adding the filtered rinsings and washings to the filtrate.
(The above steps are omitted, if the filtrate from Step No. 10 of the calcium determination is used.)
11. Add an amount of concentrated ammonium hydroxide to the filtrate equal to about 1/9 its volume and then add 10 ml. of a 10 per cent solution of disodium phosphate (21). Stir the solution vigorously for five minutes.
12. Allow to stand at least four hours, and filter the precipitate and several rinsings of the beaker onto a quantitative filter paper, being sure that all of the precipitate is transferred to the paper.

13. Wash with small portions of dilute ammonia water.
14. Ignite, cool and weigh a clean crucible.
15. Transfer the folded filter paper containing the magnesium precipitate to the crucible.
16. Ignite until almost white, cool in a desiccator and weigh.

Calculations

Gain in weight (grams) X 873.6 = p.p.m. magnesium (Mg).

Sulphates, gravimetric method

Reagents. Section II, No. (22).

1. Evaporate to dryness, in an evaporating dish on a water bath, 250 ml. of the sample to which a few drops of concentrated hydrochloric acid have been added.
2. Moisten the residue with a few drops of concentrated hydrochloric acid.
3. Add 30 ml. of distilled water, heat to boiling and filter. (More water is sometimes necessary to dissolve the calcium sulphate.)
4. Wash the dish and the paper with several small portions of distilled water, adding the filtered washings to the filtrate.
5. Heat the filtrate to boiling and add 10 ml. of a 10 per cent solution of barium chloride (22) drop by drop with constant stirring.
6. Place the mixture in a warm place for about 30 minutes.
7. Filter and wash the precipitate on the paper with warm distilled water. Be sure that all of the precipitate is transferred to the paper.
8. Ignite, cool and weigh a clean crucible.
9. Fold the filter paper containing the precipitate, place in the crucible, ignite, cool in a desiccator and weigh. (The filtrate and washings from No. 7 may be saved for the sodium and potassium determination.)

Calculations

Gain in weight of crucible (grams) X 1646.1
= p.p.m. sulphate (SO_4).

Sodium and potassium, gravimetric method

Reagents. Section II, No. (23).

1. Concentrate 250 ml. of the sample to about 50 ml. by evaporating in a dish on a water bath.
2. Add a slight excess of a saturated solution of barium hydroxide (23) and heat almost to boiling for 30 minutes. Keep the dish covered to prevent evaporation.
3. Filter, rinse the dish and wash the residue on filter paper with hot distilled water, adding the filtered rinsings and washings to the filtrate.
4. To the filtrate add ammonium hydroxide and a fresh solution of ammonium carbonate, heat on the steam bath until the precipitate settles, filter and wash.
5. Evaporate the filtrate to dryness in a dish and ignite at low red heat.
6. Take up in 10 ml. of hot distilled water, filter and wash, keeping the volume of the filtrate low.
7. Repeat Nos. 4, 5 and 6 until no precipitate forms on the addition of the reagents (ammonium hydroxide and ammonium carbonate) to the filtrate from Step No. 6.
8. Transfer the final filtrate and washings to a small platinum dish, add a few drops of concentrated hydrochloric acid and evaporate to dryness.
9. Heat to low red heat, cool and weigh.
10. Take up the residue in the dish with 10 ml. of water, filter through quantitative paper and wash the residue. Be sure all of the precipitate is transferred to the paper.
11. Transfer the filter paper to the platinum dish, ignite, cool and weigh.
12. Save the filtrate and washings for the potassium determination, if that test is to be made.

Calculations

The difference in the weights of the crucible is the weight of the combined sodium and potassium chlorides. This difference in weight X 1573.6 = p.p.m. sodium and potassium expressed in terms of sodium (Na).

Potassium, gravimetric method

Reagents. Section II, Nos. (24), (25).

1. Use the filtrate from the sodium and potassium determination or prepare the sample by the procedure given for that test.
2. Add a few drops of 1 to 3 sulphuric acid and 1 ml. of 10 per cent platinic chloride solution (24) for each 30 mg. of combined chlorides.
3. Evaporate almost to dryness on the water bath, remove the dish and allow it to dry at room temperature.
4. To the residue add about 30 ml. of 80 per cent ethyl alcohol (25), stir well so as to dissolve all of the salts soluble in the alcohol.
5. Filter and wash the precipitate with 80 per cent alcohol until the filtrate is colorless.
6. Dry the precipitate on the paper.
7. Dissolve the precipitate by washing it through the paper with small amounts of hot distilled water catching the filtrate in a platinum dish which had previously been ignited and weighed.
8. Evaporate the solution to dryness, dry for a few minutes at 103°C, cool in a desiccator and weigh.

Calculations

Difference in weight X 0.3067 = weight of KCl.

Weight of combined NaCl and KCl = weight of KCl
= weight of NaCl.

Weight of KCl (grams) X 2097.6 = p.p.m. potassium (K).

Weight of NaCl (grams) X 1573.6 = p.p.m. sodium (Na).

Scheme for the mineral analysis of water

Reagents. Section II, Nos. (16), (17), (18), (19), (20), (21), (22), (13), (14), (2), (3), (4).

Note

The following scheme has been prepared for the use of those wishing to make what might be termed a "complete mineral analysis" of water. In this scheme the methods given are combined so as to

follow step by step in the separation and quantitative determination of each element. The analysis includes the determination of silica, iron and aluminum oxides, calcium, magnesium, sulphate, bicarbonate, chloride and total solids.

Preparation of sample

Measure accurately two 250 ml. samples of the water, add a few ml. of concentrated hydrochloric acid and evaporate to dryness in dishes over a water bath. Cool and moisten each residue with a few drops of concentrated hydrochloric acid. Add about 30 ml. of distilled water and heat to boiling. Filter through separate quantitative filter papers, washing the dishes and residues on the papers with small portions of distilled water, and adding the washings to the filtrates. The volumes of filtrates should be kept below 50 ml. Save one filtrate for the iron and aluminum oxides, and calcium and magnesium determinations and the second for the sulphate determination.

Silica (SiO_2)

Ignite, cool and weigh a platinum crucible. (Porcelain may be used.) Fold one of the filter papers from the above filtration, place it in the weighed crucible and ignite. Cool in a desiccator and weigh. Gain in weight (grams) X 4000 = p.p.m. silica (SiO_2). Discard the other filter paper and residue.

First filtrate

Iron and aluminum oxides

Add a few ml. of bromine water (16) and boil a few minutes. Add 20 ml. of 10 per cent ammonium chloride solution (17) and an excess of ammonium hydroxide. Boil for 5 minutes. Ignite, cool and weigh a porcelain crucible. Filter the solution through a quantitative filter paper, rinsing and washing the beaker and filter paper with small portions of distilled water. Save the combined filtrate and washings. Fold the paper, place in the crucible and ignite. Cool and weigh. Gain

in weight (grams) X 4000 = p.p.m. Fe_2O_3 and Al_2O_3 .

Calcium

Warm the filtrate from the iron and aluminum determination, add 10 ml. of a saturated solution of ammonium oxalate (18) drop by drop with constant stirring and set in a warm place for about 30 minutes. Filter and wash the beaker and paper with hot distilled water. Save the filtrate and washings. Pierce the filter paper and wash the precipitate into the original beaker with about 30 ml. of 2 per cent sulphuric acid (19). (Use a larger quantity of acid if necessary to dissolve the precipitate.) Heat to boiling and titrate with standard permanganate (20).

ML. of KMnO_4 X 10 = p.p.m. calcium (Ca).

Magnesium

To the filtrate saved from the calcium determination, add concentrated ammonium hydroxide in sufficient quantity to make about one-ninth its volume. Add 10 ml. of sodium acid phosphate solution (21), stir vigorously for five minutes, and allow to stand at least four hours. Ignite, cool and weigh a crucible. Filter the precipitate onto quantitative filter paper, wash with weak ammonia solution and place in the crucible. Ignite, cool and weigh.

Gain in weight (grams) X 873.6 = p.p.m. magnesium (Mg).

Second filtrate

Sulphate

Heat to boiling and add, drop by drop with constant stirring, 10 ml. of 10 per cent barium chloride solution (22). Allow the mixture to stand in a warm place with occasional stirring for 30 minutes. Filter the precipitate onto a quantitative paper and wash with several portions of warm water. Ignite, cool and weigh a crucible. Place the paper and precipitate in the crucible, ignite, cool and weigh.

Gain in weight X 1644 = p.p.m. SO₄.

Sodium and potassium

These are usually obtained by difference of the positive and negative radicles according to the method given below. If a determination is desired, the filtrate from the sulphate determination may be used with the method for sodium and potassium given on pages 20-21.

Total solids

Evaporate 100 ml. of the sample in a weighed platinum dish. Dry in the oven at 103°C for 1 hour, cool in a desiccator and weigh. Difference in weight (grams) X 10,000 = p.p.m. total solids.

Chlorides

Pipette 50 ml. of the sample into an evaporating dish. Add 1 ml. of potassium chromate (13) and titrate with standard silver nitrate (14) to the first permanent brown color.

(ml. silver nitrate - 0.2) X 10 = p.p.m. chloride (Cl).

Alkalinity

Measure 100 ml. of the sample into a flask and add 3 drops of phenolphthalein (2). If a pink color develops, titrate with 0.02 N sulphuric acid (3) until the color just disappears and record the ml. of acid used. Add 3 drops of methyl orange (4) and again titrate with standard acid to the first slight permanent change in color. Record the ml. of acid used. Calculate the alkalinity according to the method given on page 7.

Calculations

To calculate sodium and potassium.

1. Find the reacting values (R) as follows:

Positive elements

p.p.m. Ca X 0.0499 = R of Ca.

p.p.m. Mg X 0.0822 = R of Mg.

p.p.m. Fe X 0.0358 = R of Fe.

p.p.m. Al X 0.1107 = R of Al.

Negative Elements

$$\text{p.p.m. } \text{HCO}_3 \times 0.0164 = R \text{ of } \text{HCO}_3.$$

$$\text{p.p.m. } \text{CO}_3 \times 0.0333 = R \text{ of } \text{CO}_3.$$

$$\text{p.p.m. } \text{SO}_4 \times 0.0208 = R \text{ of } \text{SO}_4.$$

$$\text{p.p.m. } \text{Cl} \times 0.0282 = R \text{ of } \text{Cl}.$$

2. Add the R values.

3. (Sum of negative R values - sum of positive R values) X 23 = p.p.m. sodium and potassium expressed in terms of sodium.

Example

A water analysis showed the following results:

$$\text{Ca} = 131.0 \text{ p.p.m.} \quad \text{HCO}_3 = 420.0 \text{ p.p.m.}$$

$$\text{Mg} = 46.5 \quad " \quad \text{CO}_3 = \text{none}$$

$$\text{Fe} = 0.8 \quad " \quad \text{SO}_4 = 111.0 \quad "$$

$$\text{Al} = 1.8 \quad " \quad \text{Cl} = 162.5 \quad "$$

To calculate sodium and potassium:

$$131 \times 0.0499 = 6.537 \quad 420 \times 0.0164 = 6.888$$

$$46.5 \times 0.0822 = 3.822 \quad 0.0 \times 0.0333 = 0.0$$

$$0.8 \times 0.0358 = 0.029 \quad 111 \times 0.0208 = 2.309$$

$$1.0 \times 0.1107 = \underline{0.111} \quad 162 \times 0.0282 = \underline{4.587}$$

$$10.499 \quad \quad \quad 13.784$$

$$(13.784 - 10.499) \times 23 = 75.6 \text{ p.p.m. Na and K in terms of Na.}$$

Total and residual iron, colorimetric method

Reagents. Section II, Nos. (26), (27), (28), (29).

1. Evaporate to dryness on a water bath 100 ml. of the sample containing a few drops of concentrated hydrochloric acid. (The residue from the total solids determination or that from the iron and aluminum oxides determination may be used.)
2. Cool the dish and add 1 ml. of dilute hydrochloric acid (1 volume of concentrated hydrochloric acid to 3 of water).
3. Warm on the water bath making sure that the hot acid comes in contact with all of the residue.
4. Add 10 ml. of distilled water and filter into a 100 ml. Nessler tube rinsing the dish and paper with distilled water.

5. If permanent standards (26) are available, proceed to No. 6. If not, prepare temporary standards by measuring 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 ml. of standard iron solution (27) into respective 100 ml. Nessler tubes. Add about 80 ml. of distilled water and 5 ml. of dilute hydrochloric acid to each.
6. Add two drops of potassium permanganate (28) to the tube containing the sample and to each standard.
7. Allow to stand for 5 minutes and if the color does not persist, add more permanganate.
8. Dilute the sample and standards to the mark.
9. Add 5 ml. of thiocyanate solution (29) to each tube and compare the colors immediately, recording the standard having a color nearest that of the sample.

Calculations

$$\frac{\text{ml. standard iron} \times 100}{\text{ml. of sample}} = \text{p.p.m. Fe}$$

Ferrous and ferric iron

Reagents. Section II, Nos. (30), (31), (32).

1. Prepare color standards by placing in each of eight 100 ml. Nessler tubes, 75 ml. of freshly boiled and cooled distilled water, 10 ml. of dilute sulphuric acid (30) and 15 ml. of ferricyanide solution (31).
2. Place in a ninth tube 50 ml. of the sample, 10 ml. of dilute sulphuric acid, 15 ml. of ferricyanide solution and dilute to the mark with freshly boiled and cooled distilled water.
3. Add to the eight standard tubes 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 ml. respectively of standard ferrous iron solution (32).
4. Mix and compare the blue color which develops in the sample with that of the standards recording the standard having a color nearest that of the sample. (If no color develops in the sample, no ferrous iron is present.)

Calculations

$$\frac{\text{ml. standard ferrous iron} \times 100}{\text{ml. of sample}} = \text{p.p.m. ferrous iron.}$$

$$\text{P.p.m. total iron} - \text{p.p.m. ferrous iron} = \text{p.p.m. ferric iron.}$$

Manganese, colorimetric method

Reagents. Section II, Nos. (33), (34), (35).

1. Make up standards by placing 0.2, 0.4, 0.6, 0.8, 1.0, and 1.5 ml. of standard manganous sulphate solution (33) into 250 ml. Erlenmeyer flasks and adding 50 ml. of distilled water.
2. Measure 100 ml. of the sample into a similar flask.
3. Add 2 ml. of 1 to 1 nitric acid (34) to the sample and each standard.
4. Heat the sample and standards to boiling.
5. Determine the volume of silver nitrate solution (35) necessary to precipitate the chlorides by titrating a separate portion of the sample as described in the chloride determination on pages 13 and 14.
6. Add 1 ml. of silver nitrate solution to each standard and 1 ml. more than the volume of silver nitrate as determined in No. 5 to the sample.
7. Shake and heat the flask containing the sample.
8. Filter the sample and rinsings into an Erlenmeyer flask, washing the filter paper with distilled water.
9. Add about 0.5 grams of ammonium persulphate crystals to each flask, (standards and sample), mix and warm 10 minutes.
10. Transfer to 100 ml. Nessler tubes, make up to the mark with distilled water, and compare the colors, recording the standard having the color nearest that of the sample.

Calculations

$$\frac{\text{ml. standard manganous solution} \times 100}{\text{ml. of sample}} = \text{p.p.m. Mn.}$$

Residual alum (aluminum), colorimetric method

Reagents. Section II, Nos. (36), (37), (38), (39), (40).

1. Prepare standards in 200 ml. phosphoric acid flasks (Erlenmeyer flasks may be used) by diluting 1, 2, 3, up to 8 ml. of the standard alum solution (36) to 50 ml. with distilled water. Permanent standards (37) may be used.
2. Place 50 ml. of the sample into a similar flask.
3. To each flask add 1 ml. of alizarin red S solution (38) and boil for 2 minutes.
4. Neutralize with sodium carbonate solution (39) to just barely purple by adding the solution drop by drop.
5. Add exactly 0.5 ml. excess of the carbonate solution, boil 2 minutes, and make up to 50 ml. with distilled water. (The latter may be done in Nessler tubes.)
6. Add 1 ml. of acetic acid solution (40), let stand 1 minute and compare the colors, recording the standard nearest the color of the sample.

Calculations

$$\frac{\text{ml. standard alum} \times 10}{\text{ml. of sample}} = \text{p.p.m. alum as Al}_2\text{O}_3.$$

Residual chlorine, o-tolidine method

Reagents. Section II, Nos. (66), (67).

1. Place 100 ml. of the sample in a 100 ml. Nessler tube having the graduation 300 mm. from the bottom.
2. Add 1 ml. of o-tolidine reagent (66) and mix.
3. Allow the tube to stand in a dark place for 5 minutes.
4. Compare the color which develops with that of permanent standards (67).

Residual chlorine, starch-iodide method

Reagents. Section II, Nos. (60), (68).

1. Place 200 ml. of the sample in an Erlenmeyer flask.

2. Add a small crystal of potassium iodide and 1 ml. of concentrated hydrochloric acid.
3. Add 1 ml. of starch solution (60). A blue color shows the presence of chlorine.
4. For a quantitative estimation, titrate the solution with 0.001 N sodium thiosulphate solution (68) until the blue color just disappears. Record the ml. of thiosulphate used.

Calculations

$$\text{ml. of } 0.001 \text{ N thiosulphate} \times 0.1773 = \text{p.p.m. residual chlorine.}$$

Color

Reagents. Section II, No. (41).

1. Fill a 100 ml. Nessler tube to the mark with the water to be tested.
2. Compare this color with that of standards (41) by looking vertically down through the tubes at a white surface.
3. If the color is greater than that of the standards, the water should be diluted with distilled water until within the range.

Calculations

$$\frac{\text{ml. of standard platinum solution} \times 500}{\text{ml. of sample}} = \text{color.}$$

Turbidity

Reagents. Section II, Nos. (42), (43).

For turbidities above 25 use the Jackson turbidimeter as follows:

1. Before lighting the standard candle, remove such portion of the charred part of the string as is easily broken off with the fingers. Do not keep the candle lighted for more than a few minutes at a time.
2. See that the candle is at its full height in the holder.
3. Pour the water to be tested into the tube until the image of the candle flame just disappears from view. The water should be poured very slowly after the image becomes only faintly visible.

4. Read the turbidity from the scale on the graduated tube.

For turbidities from 2 to 25.

1. Place the sample in a liter bottle of clear glass similar to that used for the standards (42).
2. Shake the sample and each standard vigorously and compare the turbidities by looking horizontally through the bottles at some object. Note the distinctness with which the outlines of the object can be seen.
3. Record the turbidity of the standard most nearly matching the sample.

For turbidities less than 2. Use the Baylis turbidimeter as follows:

1. Fill the tubes with the sample and allow to stand for 10 minutes until the air bubbles rise to the surface.
2. Select the standard (43) which seems to have a turbidity nearest that of the sample and place it and the tube containing the sample in the turbidimeter.
3. Compare the sample with the various standards until that having the same turbidity as the sample has been determined. (The turbidity in the tube cuts out some of the blue light. The same turbidities in the two tubes will give equal intensities of blue light.)
4. If the sample has a turbidity slightly above 2, it should be diluted in definite ratios until it comes within the range of this instrument. The turbidity is then calculated by multiplying the turbidity of the diluted sample by the dilution ratio.

Note

Directions for making the Baylis turbidimeter are given in the Journal of Industrial and Engineering Chemistry, Vol. 18, page 311 (1926).

Odor, qualitative method.

Cold odor.

1. Fill a flask about half full of the sample and cover with a watch glass.
2. Shake violently, remove the cover and smell the odor at the mouth of the flask.
3. Describe the odor as indicated below.

Hot odor.

1. Place 150 ml. of the sample in a 500 ml. Erlenmeyer flask.
2. Cover with a watch glass and heat almost to boiling.
3. Allow to cool with cover on for 5 minutes.
4. Shake vigorously, remove the cover and smell the odor.
5. Describe the odor as indicated below.

The results are expressed by using combinations of the numbers and letters given below:

0--no odor	e--earthy
1--very faint	f--fishy
2--faint	g--grassy
3--distinct	m--moldy
4--decided	M--musty
5--very strong	P--peaty
a--aromatic	s--sweetish
c--free chlorine	S--sulphide
d--disagreeable	v--vegetable

Odor, quantitative estimation

1. Boil a quantity of distilled water until free from odor and cool to room temperature.
2. Clean six or more 500 ml. Erlenmeyer flasks and remove the last traces of odor by boiling water in them for 5 minutes.
3. Discard the water and cool the flasks, covering them with watch glasses.
4. Determine the approximate odor as follows:
 - a. Place 100 ml. of odor-free water in each of two flasks.
 - b. Warm to 70°C and add to one flask 5 ml. of the sample.

- c. Shake both flasks vigorously, uncover and determine whether or not the water in the flask receiving the sample has an odor when compared with that in the other flask.
 - d. If the odor is present, repeat using a smaller sample.
 - e. If not present, add more of the sample to the water in the flask until the odor is present.
5. Knowing the approximate odor, a more accurate determination is made as follows:
- a. Add 100 ml. of the odor-free water to each of the several flasks.
 - b. Cover with watch glasses and warm to 70°C.
 - c. To the first five flasks add increasing volumes of the sample, taking in the value determined by the approximate method. For example, if the odor was found with 5 ml. of the sample in the approximate method, add 3, 4, 5, 6, and 7 ml. respectively to the five flasks.
 - d. Shake vigorously and determine the flask in which the odor first appears.

Note

If more than 5 ml. are required, reduce the volume of odor-free water accordingly.

Calculations

$$\frac{\text{ml. odor free water} + \text{ml. of sample}}{\text{ml. of sample}} = \text{odor value.}$$

Ammonia nitrogen

Reagents. Section II, Nos. (44), (49), (45), (46), (47).

1. Clear the distillation apparatus of ammonia by boiling distilled water in it. Use a liter Kjeldahl flask.
2. Empty the flask and measure 500 ml. of the sample into it. If a smaller sample is used, make up to 500 ml. with ammonia-free water (44).
3. Add 10 ml. of phosphate buffer solution (49) and distill until almost 200 ml. are collected in a 200 ml. volumetric flask. The residue may be

- used for either the albuminoid or organic nitrogen determination.
4. Make up the distillate to 200 ml. with ammonia-free water.
 5. Mix and pipette a measured portion into a 100 ml. Nessler tube making up to the mark with ammonia-free water. The volume required must be determined by trial. If the color produced by this volume does not come within the range of the standards, use a volume which will.
 6. If permanent ammonia standards (45) are available, proceed to Step No. 7. If not, make up temporary standards by adding 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.7, 2.0, 2.5, and 3.0 ml. of standard ammonium chloride solution (46) to 100 ml. Nessler tubes and diluting to the mark with ammonia-free water.
 7. Add 2 ml. of Nessler reagent (47) to the sample and to each temporary standard, allow to stand 10 minutes and compare the colors. Record the standard having the color nearest that of the sample.

Calculations

$$\frac{\text{ml. of standard } \text{NH}_4\text{Cl} \times 2000}{\text{ml. used in Step No. 5} \times \text{ml. of sample}} = \text{p.p.m.}$$

ammonia nitrogen as N.

$$\text{P.p.m. ammonia as N} \times 1.216 = \text{p.p.m. ammonia as } \text{NH}_3.$$

Albuminoid nitrogen

Reagents. Section II, Nos. (45), (46), (47), (48).

1. Boil 500 ml. of the sample in a Kjeldahl flask until the volume is reduced to about 300 ml.
2. Cool and add 50 ml. of alkaline potassium permanganate (48).
3. Clear the distillation apparatus of ammonia by boiling distilled water in it.
4. Connect the Kjeldahl flask and distill until almost 200 ml. of distillate is collected in a 200 ml. volumetric flask.

5. Make up to the mark with ammonia-free water and mix well.
6. Pipette a measured portion into a 100 ml. Nessler tube and make up to the mark with ammonia-free water. The volume used will vary and must be determined by trial.
7. If permanent ammonia standards (45) are available, proceed to Step No. 8. If not, make up temporary standards by adding 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.7, 2.0, 2.5, and 3.0 ml. of standard ammonium chloride (46) to 100 ml. Nessler tubes and making up to the mark with ammonia-free water.
8. Add 2 ml. of Nessler reagent (47) to the sample and to each temporary standard.
9. After standing 10 minutes, compare the colors and record the standard having a color nearest that of the sample.

Calculations

$$\begin{array}{r} \text{ml. standard } \text{NH}_4\text{Cl} \times 2000 \\ \hline \text{ml. portion used in Step No. 6} \times \text{ml. of sample} \\ = \text{p.p.m. albuminoid nitrogen as N.} \end{array}$$

Organic nitrogen

Reagents. Section II, Nos. (44), (45), (46), (47).

1. Boil 500 ml. of the sample in a Kjeldahl flask until the volume has been reduced to about 300 ml.
2. Add 5 ml. of concentrated sulphuric acid and a few boiling chips.
3. Mix and boil in the hood until all of the water is removed and the white fumes of sulphuric acid are evolved. Continue to boil until the solution becomes colorless or a light straw color.
4. Cool and add 300 ml. of ammonia-free water (44).
5. Make alkaline to litmus with 10 per cent sodium hydroxide.
6. Free the distillation apparatus of ammonia by boiling distilled water in it.

7. Connect the Kjeldahl flask and distill until almost 200 ml. of distillate have been collected in a 200 ml. volumetric flask.
8. Make up to the mark with ammonia-free water and mix well.
9. Pipette a measured portion into a 100 ml. Nessler tube and make up to the mark with ammonia-free water. The amount used will vary and must be determined by trial.
10. If permanent ammonia standards (45) are available, proceed to Step No. 11. If not, make up temporary standards by adding 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.7, 2.0, 2.5, and 3.0 ml. of standard ammonium chloride (46) to 100 ml. Nessler tubes and making up to the mark with ammonia-free water.
11. Add 2 ml. of Nessler reagent (47) to the sample and to each temporary standard.
12. After standing for 10 minutes, compare the colors and record the standard having a color nearest that of the sample.

Calculations

$$\frac{\text{ml. of standard NH}_4\text{Cl} \times 200}{\text{ml. portion used in Step No. 9} \times \text{ml. sample}} = \text{p.p.m. organic nitrogen as N.}$$

Nitrite nitrogen

Reagents. Section II, Nos. (50), (51), (52).

1. Place 100 ml. of the sample into a 100 ml. Nessler tube. (If the nitrite content proves to be high, a smaller volume diluted to 100 ml. with distilled water may be used.)
2. Prepare standards by adding 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.7, 2.0 and 2.5 ml. of standard sodium nitrite solution (50) to 100 ml. Nessler tubes and diluting to the mark with distilled water.
3. Add 2 ml. of sulfanilic acid solution (51) and 2 ml. of a-naphthylamine acetate solution (52) to the sample and to each standard.

4. Mix and after 10 minutes compare the colors, selecting the standard having a color nearest that of the sample.

Calculations

$$\frac{\text{ml. standard NaNO}_2 \times 0.5}{\text{ml. of sample}} = \text{p.p.m. nitrite nitrogen as N.}$$

$$\text{P.p.m. nitrite nitrogen as N} \times 3.284 = \text{p.p.m. nitrite as NO}_2.$$

Nitrate nitrogen, phenoldisulphonic acid method

Reagents. Section II, Nos. (3), (53), (15), (54), (55), (56).

1. Determine the number of ml. of 0.02 N sulphuric acid (3) necessary to neutralize the methyl orange alkalinity of 100 ml. of the sample. See page 6. Also, determine the number of ml. of silver sulphate solution (53) necessary to precipitate the chlorides in 100 ml. of sample. See page 14.
2. If the sample is highly colored, stir a 200 ml. portion with a small portion of aluminum hydroxide (15) and filter.
3. Pipette 100 ml. of the sample or the clarified filtrate into an evaporating dish and add the quantity of 0.02 N sulphuric acid as determined in Step No. 1.
4. If less than 3 ml. of the silver sulphate solution was required in Step No. 1, proceed to Step No. 5. If more than 3 ml. were required, add slightly less than the volume required to the sample in the evaporating dish. Add a small amount of aluminum hydroxide (15), mix, and filter into a second dish.
5. Evaporate the sample from Step 3 or the filtrate from Step 4 to dryness on the water bath.
6. Add 3 ml. of phenoldisulphonic acid (54) and rub in well with a glass rod to insure contact of the acid with the residue.

7. Dilute with 20 ml. of distilled water and add slowly with stirring a solution of sodium hydroxide (55) until the maximum yellow color is developed. Not more than 6 ml. will be required. If no color develops, nitrate is absent.
8. Filter into a 100 ml. Nessler tube and rinse the dish and paper adding the rinsings to the tube until all of the colored solution has been transferred. Dilute to the mark with distilled water.
9. Prepare standards by adding 0.2, 0.5, 0.75, 1.0, 3.0, 5.0, 10, 20, 30, and 40 ml. of the standard nitrate solution (56) to 100 ml. Nessler tubes, diluting to the mark and adding 2 ml. of sodium hydroxide (55) to each tube.
10. Compare the colors, selecting the standard having a color nearest that of the sample.

Calculations

$$\frac{\text{ml. of standard nitrate} \times 10}{\text{ml. of sample}} = \text{p.p.m. nitrate}$$

nitrogen as N.

$$\text{P.p.m. nitrate as N} \times 4.427 = \text{p.p.m. nitrate as } \text{NO}_3.$$

Dissolved oxygen, Winkler method

Reagents. Section II, Nos. (57), (58), (59), (60).

Note

This method may be used for the majority of dissolved oxygen determinations made in the water laboratory. In cases where a water high in iron, nitrites, or organic matter is encountered, the Rideal-Stewart modification given on page 38 should be used.

1. Collect the sample in an 8-ounce glass-stoppered bottle being very careful to avoid contact of the sample with air. (See "Sampling for dissolved oxygen", page 174.) The bottle should be completely filled.
2. Immediately after collection, add 1 ml. of manganese sulphate solution (57) by means of pipette, dipping the end of the pipette just below the surface of the water.

3. Add 1 ml. of alkaline potassium iodide solution (58) in a similar manner.
4. Insert the stopper and mix by inverting the bottle several times.
5. Allow the precipitate to settle halfway and mix again.
6. Again allow the precipitate to settle halfway.
7. Add 1 ml. of concentrated sulphuric acid. Insert the stopper at once after the addition of the acid, and mix as before.
8. Allow the solution to stand at least 5 minutes.
9. Withdraw 100 ml. of the solution into an Erlenmeyer flask and immediately add 0.025 N sodium thiosulphate (59) drop by drop from a burette until the yellow color almost disappears.
10. Add about 1 ml. of starch solution (60) and continue the addition of the thiosulphate until the blue color just disappears. Record the ml. of thiosulphate used. (Disregard any return of the blue color.)

Calculations

ml. of 0.025 N sodium thiosulphate X 2 = p.p.m.
dissolved oxygen.

Dissolved oxygen, Rideal-Stewart modification

Reagents. Section II, Nos. (57), (58), (59), (60), (61), (62).

1. Collect the sample in an 8-ounce glass-stoppered bottle being careful to avoid contact of the sample with the air. See "Sampling for dissolved oxygen", page 174. The bottle should be completely filled.
2. Immediately after collecting, add 0.7 ml. of concentrated sulphuric acid and 1 ml. of potassium permanganate (61) by means of pipettes, dipping them just below the surface of the water in the bottle.
3. Insert the stopper and mix by inverting the bottle several times.

4. If the color of the permanganate does not last for 20 minutes, add 1 ml. more. If this is not sufficient, use a stronger solution.
5. After 20 minutes, add 1 ml. of potassium oxalate (62), insert the stopper and mix.
6. After the color has disappeared, add 1 ml. of manganous sulphate (57) and 3 ml. of alkaline potassium iodide (58), insert the stopper and mix.
7. Allow the precipitate to settle halfway and mix again.
8. Again allow the precipitate to settle halfway.
9. Add 1 ml. of concentrated sulphuric acid, insert the stopper and mix immediately. Do not allow the bottle to stand open after the addition of the acid.
10. Allow the solution to stand at least 5 minutes. (The solution may stand several hours in this condition without harm.)
11. Rapidly withdraw 100 ml. of the solution into an Erlenmeyer flask and add 0.025 N sodium thiosulphate (59) drop by drop from a burette until the yellow color almost disappears.
12. Add 1 ml. of starch solution (60) and continue the addition of the thiosulphate until the blue color just disappears. Record the ml. of thiosulphate used. Disregard any return of the blue color.

Calculations

Ml. of 0.025 N sodium thiosulphate X 2 = p.p.m.
dissolved oxygen.

Oxygen consumed

Reagents. Section II, Nos. (63), (64), (65).

1. Pipette 100 ml. of the sample into a 250 ml. Erlenmeyer flask.
2. Add 10 ml. of dilute sulphuric acid (63) and 10 ml. of standard potassium permanganate (65).
3. Heat in a boiling water bath for exactly 30 minutes keeping the water in the bath above the level of the solution in the flask.

4. If the solution becomes faintly colored, repeat the above using a smaller sample diluted to 100 ml. with distilled water.
5. After 30 minutes in the water bath, add 10 ml. of standard ammonium oxalate (64).
6. Titrate while hot with standard potassium permanganate to the first pink coloration. Record the ml. of permanganate used.

Calculations

$$\frac{\text{ml. of potassium permanganate used in Step 6} \times 100}{\text{ml. of sample}} = \text{p.p.m. oxygen consumed.}$$

Lime, per cent oxide or hydroxide

Reagents. Section II, Nos. (2), (4), (95).

1. Pulverize the sample and sift through a screen containing 50 openings per linear inch.
2. Weigh 0.5 grams of the sample into a liter glass-stoppered bottle.
3. Add 500 ml. of freshly boiled and cooled distilled water.
4. Shake occasionally for a period of about 1 hour and allow to settle overnight.
5. Pipette 50 ml. of the clear supernatent liquor into a 250 ml. Erlenmeyer flask, add 3 drops of phenolphthalein (2) and titrate with 0.1 N sulphuric acid (95) until the pink color just disappears. Record the ml. of acid used.
6. Add 3 drops of methyl orange (4) and again titrate with the 0.1 N acid to the first change in color. Record the ml. of acid used.

Calculations

Let T = total ml. of acid used for both the phenolphthalein and methyl orange titrations.

Let P = ml. of acid used for the phenolphthalein titration.

$(2P - T) \times 7.4$ = per cent calcium hydroxide, if hydrated lime is used.

$(2P - T) \times 5.6$ = per cent calcium oxide if quick-lime is used.

Lime, per cent calcium

Reagents. Section II, Nos. (17), (18).

1. Partly fill a weighing bottle with the lime and, with the stopper removed, dry in the 103°C oven for 1 hour.
2. Cool the weighing bottle and contents in a desiccator and weigh. Pour about 0.5 grams of the lime into a beaker and again weigh the bottle and contents. The difference in weight is the weight of the dry lime sample used.
3. Add about 30 ml. of 1 to 1 hydrochloric acid and heat gently for about 5 minutes.
4. Filter and rinse the beaker and paper with small portions of hot distilled water, adding the filtered rinsings to the filtrate. (The paper may be ignited in a weighed crucible and reported as insoluble matter.)
5. Add 10 ml. of 10 per cent ammonium chloride solution (17) to the filtrate and make alkaline to litmus with concentrated ammonium hydroxide.
6. If a precipitate of iron and aluminum oxides forms, filter and wash the beaker and paper with distilled water, adding the filtered washings to the filtrate.
7. Heat to boiling and add slowly with stirring 20 ml. of a saturated solution of ammonium oxalate (18).
8. Allow to stand in a warm place for 30 minutes.
9. Ignite, cool, and weigh a crucible.
10. Filter the precipitate onto a quantitative filter paper and wash well with small portions of distilled water.
11. Test the filtrate with a few drops of ammonium oxalate to make sure all of the calcium is precipitated.
12. Place the paper and precipitate in the weighed crucible and ignite to bright red heat for 30 minutes, cool in the desiccator and weigh. Repeat the ignition until no further loss in weight is secured.

Calculations

If hydrated lime is used:

$$\frac{\text{Gain in weight (grams)} \times 132}{\text{weight of sample (grams)}} = \text{per cent Ca(OH)}_2.$$

If quicklime is used:

$$\frac{\text{Gain in weight (grams)} \times 100}{\text{weight of sample (grams)}} = \text{per cent CaO}.$$

Soda ash, per cent sodium carbonate

Reagents. Section II, Nos. (4), (97).

1. Dissolve 0.53 grams of the sample in boiled distilled water in a 100 ml. volumetric flask.
2. Make up to the mark with boiled distilled water and mix.
3. Pipette 50 ml. of the solution into an Erlenmeyer flask and add 3 drops of methyl orange (4).
4. Titrate with 0.1 N sulphuric acid (97) to the first slight permanent change in color. Record the ml. of acid used.

Calculations

$$\text{Ml. of 0.1 N acid} \times 2 = \text{per cent Na}_2\text{CO}_3.$$

Alum, per cent aluminum oxide

Reagents. Section II, No. (17).

1. Weigh about 0.5 grams of the alum into a beaker and dissolve in about 100 ml. of distilled water.
2. Filter off any insoluble residue, rinse the beaker and paper with distilled water, and add the filtered rinsings to the filtrate.
3. Add 10 ml. of 10 per cent ammonium chloride (17) and make alkaline to litmus with concentrated ammonium hydroxide.
4. Cover the beaker with a cover glass and boil gently for about 10 minutes.
5. Filter onto a quantitative filter paper and wash the beaker and paper several times with hot distilled water.
6. Ignite, cool, and weigh a crucible.

7. Fold the paper, place it in the weighed crucible and after drying ignite at a bright red heat for at least 10 minutes.

8. Cool in a desiccator and weigh.

Calculations

$$\frac{\text{Gain in weight (grams)} \times 100}{\text{weight of sample (grams)}} = \text{per cent Al}_2\text{O}_3.$$

$$\text{Per cent Al}_2\text{O}_3 \times 3.35 = \text{per cent Al}_2(\text{SO}_4)_3.$$

$$\text{Per cent Al}_2\text{O}_3 \times 6.537 = \text{per cent Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}.$$

Mechanical analysis of sand

Sampling: Samples should be carefully taken so as to be representative of the body of sand. See "Sampling" in Appendix, page 175.

Weight and Moisture

1. Weigh a dry, eight-ounce, wide-mouthed, glass-stoppered bottle on the trip scales to the nearest 0.1 gram. Let B = the weight of the bottle in grams.
2. Fill the bottle with water, insert the stopper and reweigh. Let BW = the weight of the bottle and water in grams.
3. Dry the bottle, fill with the sand, insert the stopper, and reweigh. Let BS = weight of bottle and sand in grams.
4. Weigh an evaporating dish to the nearest 0.1 gram. Let E = the weight of the dish in grams.
5. Add 100 grams of the sand to the dish.
6. Dry in a 103°C oven to constant weight. Let EDS = weight of evaporating dish and dried sand in grams.

Calculations

$$\text{Density} = \frac{\text{BS} - \text{B}}{\text{BW} - \text{B}} = \text{D}.$$

$$\text{Weight per cubic foot} = 62.4 \times \text{D}.$$

$$\text{Per cent moisture} = 100 + \text{E} - \text{EDS}.$$

$$\text{Weight of dried sand} = \text{EDS} - \text{E} = \text{DS} \text{ (dried sand).}$$

Sieve analysis for sizes.

1. Place the dried sand (DS), as obtained in the preceding moisture determination, in the top of a nest of sieves (see below) and shake. The sieves may be shaken by hand or by machine.
2. Continue the shaking until no appreciable amount of sand passes. A five minute period is commonly used.
3. Weigh the amount in grams retained on each sieve.

Calculations

Calculate the per cent by weight passing each sieve as follows: Let W = the weight of sand retained on the sieve in question plus that retained on all coarser sieves (those above).

$$\frac{[\text{Weight of dried sand (DS)} - W]}{\text{DS}} \times 100$$

= per cent passing. Plot the values obtained on coordinate paper using the vertical scale for per cent passing and the horizontal scale for the diameter in millimeters. Draw a curve connecting the points.

Determine the point of intersection of the horizontal 10 per cent line and the curve. The value on the diameter scale of this point is the "effective size" of the sand in millimeters.

Determine the point of intersection of the horizontal 60 per cent line with the curve. The value on the diameter scale is the size in millimeters than which 60 per cent is finer.

The ratio of the diameter of the 60 per cent size to the "effective size" is the "uniformity coefficient."

$$\frac{\text{Diameter of 60 per cent size}}{\text{Diameter of effective size}} = \text{uniformity coefficient.}$$

Note

The nest of sieves may consist of a nest of Tyler sieves as follows:

Sieve No.	Size of openings mm.	Sieve No.	Size of openings mm.
60	.246	28	.589
48	.295	24	.701
42	.351	20	.833
35	.417	16	.991
32	.495	14	1.168
		10	1.651

The above tabulated sizes of sieve openings can not be depended on for accurate work. It is advisable to rate the sieves according to the following method.

Rating of sieves

1. Sieve a sample in the usual manner through a nest of sieves.
2. Take each sieve, one at a time, and shake slightly, collecting the sand grains which pass through.
3. Count out a number of these grains.
4. Weigh the number counted accurately on an analytical balance.

Calculations

Let G = weight of one grain in milligrams.

$$\frac{\text{Weight of grains in grams} \times 1000}{\text{Number of grains}} = G$$

$$\text{Diameter of sand in mm.} = 0.9 \times \sqrt[3]{G}.$$

For sands of a different specific gravity than 2.65, the following formula may be used:

$$\text{Diameter in mm.} = \sqrt[3]{\frac{1.91 G}{\text{Sp. Gr.}}}.$$

The diameter of the sieve openings may be assumed to be equal to the diameter of the sand grains obtained by the above procedure.

Part B. Sewage Analysis

Note. Numbers inclosed in parentheses, thus (3), refer to numbered reagents and solutions in Section II.

Total Solids

1. Clean an evaporating dish and place it in a 103°C oven for one hour, or if the loss on ignition determination is also to be made, ignite to low red heat in the muffle furnace or over a burner. (A platinum dish is preferred, but others may be used.)
2. Place the dish in a desiccator to cool and weigh.
3. Place the weighed dish on a steam or water bath.
4. Thoroughly mix the sample and measure out 100 ml. into a 100 ml. graduate. (Care must be taken to keep the solids in suspension while measuring.)
5. Transfer the sample to the dish. Rinse the graduate several times with small portions of distilled water and add the rinsings to the dish, being sure that all suspended matter is transferred.
6. After the sample is evaporated, dry the dish and residue in the 103°C oven for one hour, cool in the desiccator and weigh.

Calculations

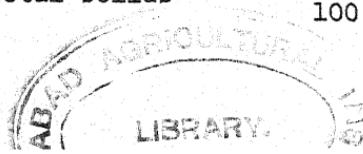
$$\frac{\text{Increase in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m.}$$

total solids.

Example

Sample	No. 1
Wt. of dish and residue (100 ml.)	48.3424 gms.
Wt. of dish	<u>48.2540</u> "
Wt. of solids	0.0884 "

$$\text{Total solids } \frac{0.0884 \times 1,000,000}{100} = 884 \text{ p.p.m.}$$



Loss on ignition

1. Place the evaporating dish and residue from the total solids determination in the muffle furnace or ignite over a burner at low red heat until the ash is white or nearly so.
2. Allow the dish to cool and moisten the residue with a few drops of distilled water.
3. Dry in the 103°C oven for one hour, cool in a desiccator and weigh.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m. loss}$$

on ignition.

Example

Sample	No. 1
Wt. of dish and residue (100 ml.)	48.3424 gms.
Wt. of dish and ash	<u>48.3130</u> "
Loss in weight	0.0294 "

$$\text{Loss on ignition} = \frac{0.0294 \times 1,000,000}{100} = 294 \text{ p.p.m.}$$

Suspended and dissolved solids, Gooch crucible method

Reagents. Section II, No. (1).

1. Pour about 25 ml. of asbestos emulsion (1) into a Gooch crucible.
2. Apply the suction gently until the mat is formed.
3. Wash with distilled water until no fibers of asbestos run through the filter.
4. Dry the crucible and ignite at low red heat. Cool, moisten with distilled water, dry at 103°C for one hour, cool and weigh. (Ignition and moistening may be omitted if the loss on ignition of suspended solids is not to be made.)
5. Measure 100 ml. of the well mixed sewage by means of a graduate, keeping the solids in suspension while measuring.
6. Filter the sample through the prepared Gooch crucible and also several distilled water rinsings of the graduate, being sure that all suspended matter is transferred to the crucible.

7. Dry in the 103°C oven for one hour, cool in the desiccator and weigh.

Calculations

$$\frac{\text{Increase in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m.}$$

suspended solids.

$$\begin{aligned} \text{P.p.m. total solids} - \text{p.p.m. suspended solids} \\ = \text{p.p.m. dissolved solids.} \end{aligned}$$

Example

Wt. of crucible and solids (100 ml.)	15.5999 gms.
Wt. of crucible	15.5817 "
Wt. of solids	0.0182 "

$$\text{Suspended solids} = \frac{0.0182 \times 1,000,000}{100} = 182 \text{ p.p.m.}$$

$$\text{Dissolved solids} = 884 - 182 = 702 \text{ p.p.m.}$$

Loss on ignition suspended and dissolved solids,
Gooch crucible method

1. Ignite the crucible from the suspended solids determination at low red heat.
2. Cool and moisten the ash with a few drops of distilled water.
3. Dry at 103°C for one hour, cool in the desiccator and weigh.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m. loss}$$

on ignition.

$$\begin{aligned} \text{P.p.m. loss on ignition of total solids} - \text{p.p.m.} \\ \text{loss on ignition suspended solids} = \text{p.p.m. loss} \\ \text{on ignition of dissolved solids.} \end{aligned}$$

Example

Wt. of crucible and solids (100 ml.)	15.5999 gms.
Wt. of crucible and ash	15.5889 "
Loss in weight	0.0110 "

Loss on ignition suspended solids

$$= \frac{0.0110 \times 1,000,000}{100} = 110 \text{ p.p.m.}$$

Loss on ignition dissolved solids = 294 - 110
= 184 p.p.m.

Dissolved and suspended solids, filtration method

1. Filter a portion of the sewage through a filter paper.
2. Repeat the method given for total solids using 100 ml. of the above filtrate.

Calculations

$$\frac{\text{Increase in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m.}$$

dissolved solids.

P.p.m. total solids - p.p.m. dissolved solids
= p.p.m. suspended solids.

Example

Wt. of dish and residue (100 ml.)	48.3242 gms.
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Wt. of dish	48.2540 "
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Increase in weight	0.0702 "
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$$\text{Dissolved solids} = \frac{0.0702 \times 1,000,000}{100} = 702 \text{ p.p.m.}$$

$$\text{Suspended solids} = 884 - 702 = 182 \text{ p.p.m.}$$

Loss on ignition, dissolved and suspended solids, filtration method

1. Ignite the dish and residue from the dissolved solids determination to low red heat.
2. Cool and moisten the residue with a few drops of distilled water.
3. Dry at 103°C for one hour, cool in a desiccator and weigh.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 1,000,000}{\text{ml. of sample}} = \text{p.p.m. loss}$$

on ignition dissolved solids.

Loss on ignition total solids - loss on ignition dissolved solids = loss on ignition suspended solids.

Example

Wt. of dish and residue (100 ml.)	48.3242 gms.
Wt. of dish and ash	48.3058 "
Loss in weight	0.0184 "
Loss on ignition of dissolved solids	
= $\frac{0.0184 \times 1,000,000}{100}$	184 p.p.m.

$$\text{Loss on ignition of suspended solids} = 294 - 184 \\ = 110 \text{ p.p.m.}$$

Settleable solids

1. Fill an Imhoff cone to the liter mark with the thoroughly mixed sewage. (For activated sludge a liter graduate should be used in place of the cone.)
2. Allow the solids to settle quietly for two hours. (A one hour period is used for activated sludge.)
3. Read the volume of solids settled in the tip of the cone or the bottom of the graduate.

Calculations

Report the results as ml. per liter.

Solids in activated sludge

1. Fill a 500 ml. graduated cylinder to the 500 ml. mark with the activated sludge (or the aeration tank contents).
2. Add 1 ml. of ferric chloride solution (102) and mix rapidly.
3. Stir slowly by means of a long rod for a few minutes.
4. Weigh a 12.5 cm. filter paper to the nearest 0.1 gram on the trip scale.
5. Place the filter paper in a Buechner funnel (126 mm. inside diameter) and filter the sludge, applying the vacuum as required.
6. Before the sludge is dry, scrape the adhering sludge from the sides of the funnel onto the paper by means of a spatula.

7. Carefully remove the paper and sludge from the funnel, place in a 103°C oven for one hour, and reweigh to the nearest 0.1 gram.

Calculations

(Wt. of paper and sludge (grams) - wt. of paper
 $\div 0.1 \times 0.2$ = per cent solids.

(Wt. of paper and sludge (grams) - wt. of paper - 0.1) X 2000 = p.p.m. suspended solids.

Settleable solids in ml. per liter X 10 = sludge
p.p.m. suspended solids index.

Alkalinity

Reagents. Section II, Nos. (2), (3), (4).

1. Pipette 100 ml. of the sample into one Erlenmeyer flask and the same quantity of distilled water into another.
 2. Add four drops of phenolphthalein (2) to each.
 3. If the sample becomes pink, add 0.02 N sulphuric acid (3) from a burette until the pink color just disappears and record the number of ml. of acid used.
 4. Add two drops of methyl orange (4) to each flask.
 5. If the sample becomes yellow, add 0.02 N sulphuric acid until the first difference in color is noted when compared with the distilled water. The end-point is a slight orange tinge. Record the ml. of acid used.

Calculations

Total alkalinity as CaCO_3 = total ml. acid used
 $\times 10.$

Differentiation of OH, CO₃, and HCO₃ alkalinities.

Let P = the ml. of 0.02 N acid used for the titration with phenolphthalein and T = the ml. of acid used for the total titration (phenolphthalein and methyl orange).

There are five possible conditions as follows:

- $$1, P = T$$

Hydroxide (p.p.m.) = P X 10.

2. P greater the 1/2 T.

$$\text{Hydroxide (p.p.m.)} = (2P - T) \times 10.$$

$$\text{Normal carbonate (p.p.m.)} = 2(T - P) \times 10.$$

$$3. P = 1/2 T$$

Normal carbonate (p.p.m.) = $T \times 10$.

$$4. P \text{ less than } 1/2 T$$

Normal carbonate (p.p.m.) = $2P \times 10$

Bicarbonate (p.p.m.) = $(T - 2P) \times 10$.

$$5. P = 0$$

Bicarbonate (p.p.m.) = $T \times 10$

All above results are in terms of CaCO_3 .

For illustrative example see page 7.

Acidity

Reagents. Section II, Nos. (2), (5).

1. Pipette 100 ml. of the sample into one Erlenmeyer flask and the same quantity of distilled water into another.
2. Add 4 drops of phenolphthalein (2) to each.
3. Add 0.02 N sodium hydroxide (5) from a burette to the sample until the first permanent pink color appears, comparing with the distilled water. Record the ml. of sodium hydroxide used.

Calculations

ml. of 0.02 N NaOH $\times 10$ = p.p.m. total acidity expressed in terms of CaCO_3 .

Hydrogen-ion concentration (pH), colorimetric method

There are a number of different types of colorimetric pH outfits on the market each requiring a slightly different procedure in making the test. The general method below is adapted to most of these outfits.

1. Place 10 ml. of the sample into each of the two or three tubes provided.
2. To one tube add the designated quantity of indicator solution. (The other tubes do not receive the indicator.)
3. Place the tubes in the comparator in such a manner that the color standards are opposite the tubes not containing the indicator. The color comparison must be made by looking through the same thickness of liquid having the same color and turbidity as the sample.

4. Compare the colors and read the pH of the tube having a color nearest that of the sample.

Note

If the quinhydrone electrometric method is to be used see page 68 under sludge analysis.

Dissolved oxygen, Winkler method

Reagents. Section II, Nos. (57), (58), (59), (60).

Note

This method may be used for the majority of dissolved oxygen determinations made in the sewage laboratory. In cases where a sample high in iron, nitrites or organic matter is encountered, the Rideal-Stewart modification should be used.

1. Collect the sample in an 8-ounce glass-stoppered bottle being very careful to avoid contact of the sample with air. (See "Sampling for dissolved oxygen", page 174.) The bottle should be completely filled.
2. Immediately after collection, add 1 ml. of managanous sulphate solution (57) by means of a pipette, dipping the end of the pipette just below the surface of the liquid.
3. Add 1 ml. of alkaline potassium iodide solution (58) in a similar manner.
4. Insert the stopper and mix by inverting the bottle several times.
5. Allow the precipitate to settle halfway and mix again.
6. Again allow the precipitate to settle halfway.
7. Add 1 ml. of concentrated sulphuric acid. Insert the stopper at once after the addition of the acid and mix as before.
8. Allow the solution to stand at least 5 minutes.
9. Rapidly withdraw 100 ml. of the solution into an Erlenmeyer flask and add 0.025 N sodium thiosulphate (59) drop by drop from a burette until the yellow color almost disappears.
10. Add about 1 ml. of starch solution (60) and continue the addition of the thiosulphate until the

blue color just disappears. Record the ml. of thiosulphate used. Disregard any return of the blue color.

Calculations

ml. of 0.025 N thiosulphate X 2 = p.p.m. dissolved oxygen.

Dissolved oxygen, Ridel-Stewart modification

Reagents. Section II, Nos. (57), (58), (59), (60), (61), (62).

1. Collect the sample in an 8-ounce glass-stoppered bottle being careful to avoid contact of the sample with air. (See "Sampling for dissolved oxygen", page 174.) The bottle should be completely filled.
2. Immediately after collecting, add 0.7 ml. of concentrated sulphuric acid and 1 ml. of potassium permanganate (61) by means of pipettes, dipping them just below the surface of the liquid in the bottle.
3. Insert the stopper and mix by inverting the bottle several times.
4. If the color of the permanganate does not last for 20 minutes, add 1 ml. more. If this is not sufficient, use a stronger solution.
5. After 20 minutes, add 1 ml. of potassium oxalate (62), insert the stopper and mix.
6. After the color has disappeared, add 1 ml. of manganese sulphate (57) and 3 ml. of alkaline potassium iodide (58), insert the stopper and mix.
7. Allow the precipitate to settle halfway and mix again.
8. Again allow the precipitate to settle halfway.
9. Add 1 ml. of concentrated sulphuric acid, insert the stopper and mix immediately. Do not allow the bottle to stand open after the addition of the acid.
10. Allow the solution to stand at least 5 minutes. (The solution may stand several hours in this condition without harm.)

11. Rapidly withdraw 100 ml. of the solution into an Erlenmeyer flask and add 0.025 N sodium thiosulphate (59) drop by drop from a burette until the yellow color almost disappears.
12. Add 1 ml. of starch solution (60) and continue the addition of the thiosulphate until the blue color just disappears. Record the ml. of thiosulphate used. Disregard any return of the blue color.

Calculations

ml. of 0.025 N sodium thiosulphate X 2 = p.p.m.
dissolved oxygen.

Biochemical oxygen demand

Reagents. Section II, Nos. (70), (71).

1. Clean the desired number of 8-ounce, glass-stoppered bottles by filling them with cleaning solution (70) and after standing for some time rinsing with tap water until the solution is entirely removed. Allow them to drain and fit the neck of the bottle with a water seal made of radiator hose or other heavy rubber tubing.
2. Fill one bottle completely with diluting water (71), insert the stopper tightly and fill the seal.
3. Make up dilutions for incubation by either (a) or (b).
 - (a) For dilutions to contain 1 per cent or more of sample. Measure the capacity of the bottles (72). Fill each about halfway with diluting water (71) by means of a siphon. Add the quantity of well mixed sewage or waste necessary to make the desired dilution and then fill completely with the diluting water. Insert the stopper tightly without entraining air bubbles and fill the seal.
 - (b) For dilutions to contain less than 1 per cent of the sample. Siphon about 500 ml. of diluting water into a liter graduate. (The graduate must be clean.) Add the quantity of well mixed

sewage or waste necessary to make the desired dilution and fill to 1000 ml. with diluting water. Mix well with a plunger type stirring rod avoiding the entrainment of air. Syphon the well mixed dilution into one of the 8-ounce incubation bottles, tightly stopper and fill the seal.

4. Proceed by either (a) or (b).

(a) For dilutions containing less than 5 per cent of the sample. Incubate the diluting water sample and the dilutions at 20°C (\pm 1 degree) for 5 days. At the end of the incubation period make a dissolved oxygen determination on the diluting water sample and on each dilution, using the Winkler method.

Calculations

$$\frac{\text{p.p.m. D.O. diluting water} - \text{p.p.m. D.O. dilution}}{\text{per cent of sample in the dilution}} \times 100 \\ = \text{p.p.m. 5-day B.O.D.}$$

(b) For dilutions to contain more than 5 per cent of the sample. Fill two bottles with diluting water. Make up two dilutions for each percentage dilution using the method given in Step 3a. Place one diluting water sample and one sample of each percentage dilution in the 20°C incubator. Make the dissolved oxygen determinations at once on the other samples. After 5 days incubation make the dissolved oxygen determinations on the incubated samples. The difference in the D.O. of the diluting water before and after incubation is the correction for the B.O.D. of that water.

Calculations

Let A equal the D.O. of the dilution before incubation, B equal the D.O. after incubation, and C equal the correction as determined above.

$$\frac{(A - B - C) \times 100}{\text{per cent of sample in dilution}} = \text{p.p.m. 5-day B.O.D.}$$

Oxygen consumed

Reagents. Section II, Nos. (63), (64), (65).

1. Measure 50 ml. of the well mixed sewage into a 250 ml. Erlenmeyer flask using a 50 ml. graduate. (For very strong sewages or trade wastes use a smaller portion.)
2. Rinse the graduate well with distilled water, adding the rinsings to the flask and finally add distilled water to give a total volume of about 100 ml.
3. In a second flask place 100 ml. of distilled water. This water is to be used as a check.
4. To each add 10 ml. of dilute sulphuric acid (63) and 10 ml. of standard potassium permanganate solution (65).
5. Place each flask in a boiling water bath and digest for exactly 30 minutes being sure that the water in the bath is at all times above the surface of that in the flasks. Watch the color of these solutions and should they become faintly colored, repeat the digestion using a larger quantity of permanganate.
6. After 30 minutes, add 10 ml. of standard ammonium oxalate solution (64) to each flask.
7. Add drop by drop from a burette standard permanganate until the first permanent pink color is obtained and record the ml. used in each case.

Calculations

Let K = total ml. of KMnO_4 used for the sample including that added before digestion.

N = total ml. of oxalate used for the sample.

k = ml. KMnO_4 used for the distilled water.

n = ml. oxalate used for the distilled water.

$$\frac{(K - N) - (k - n) \times 100}{\text{ml. of sample}} = \text{p.p.m. oxygen consumed.}$$

Example

Total volume sample used	50 ml.
Total KMnO_4 added to sample (K)	24.4 "
Total oxalate added to sample (N)	10.0 "

Total KMnO₄ added to distilled water (k) 11.2 ml.

Total oxalate " " " " (n) 10.0 "

$$\frac{(24.4 - 10.0) - (11.2 - 10.0) \times 100}{50} = 26.4 \text{ p.p.m.}$$

Relative stability

Reagents. Section II, No. (73).

1. Fill completely to overflowing a 6 or 8-ounce glass-stoppered bottle with the sample to be tested.
2. Add 0.5 ml. of a solution of methylene blue (73) by means of a pipette, extending the tip just below the surface of the liquid in the bottle.
3. Replace the stopper so that no air bubbles are entrained beneath it.
4. Keep the bottle where the temperature is nearly constant and as near 20°C as possible.
5. Observe the bottle at least once each day and record the time necessary for the disappearance of the color.

Calculations

Read the per cent stability from the following table.

Days required for disappearance of color	Relative stability per cent
0.5	11
1.0	21
2.0	37
3.0	50
4.0	60
5.0	67
6.0	75
7.0	80
8.0	84
9.0	87
10.0	90
12.0	95

Ammonia nitrogen, direct Nesslerization

Reagents. Section II, Nos. (74), (55), (44), (45), (46), (47).

1. Place 100 ml. of the sample in a Nessler tube and add 1 ml. of a 10 per cent solution of copper sulphate (74).
2. Mix by rotating and add 1 ml. of 50 per cent sodium hydroxide (55).
3. Mix again and allow to settle.
4. Pipette a measured portion of the clear supernatent liquor (5 to 25 ml. depending upon the ammonia content) into a second Nessler tube and dilute to 100 ml. with ammonia-free water (44).
5. If permanent ammonia standards are available (45). proceed to Step 6. If not, make up temporary standards by adding 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.7, 2.0, 2.5, and 3.0 ml. of standard ammonium chloride (46) to 100 ml. Nessler tubes diluting to the mark with ammonia-free water.
6. Add 2 ml. of Nessler reagent (47) to the sample and to each temporary standard.
7. After 10 minutes, compare the colors and record the standard having a color nearest that of the sample.

Calculations

$$\frac{\text{ml. standard } \text{NH}_4\text{Cl} \times 10}{\text{ml. portion used in Step 4}} = \text{p.p.m. ammonia nitrogen as N.}$$

Albuminoid nitrogen

Reagents. Section II, Nos. (44), (45), (46), (47), (48).

1. Measure 50 ml. of the well mixed sample and 50 ml. of distilled water into a 500 ml. Kjeldahl flask.
2. Connect to the distillation apparatus and boil until the distillate is free from ammonia as shown by adding a few drops of Nessler reagent (47) to a small portion of the distillate. The volume will be reduced about one half.

3. Cool the distillate, add about 250 ml. of ammonia-free water (44) and 50 ml. of alkaline potassium permanganate (48).
4. Reconnect to the distillation apparatus and distill until almost 200 ml. of distillate is collected in a 200 ml. volumetric flask. Distillation should be at a rate of 6 to 10 ml. per minute.
5. Make the distillate up to the mark with ammonia-free water and mix well.
6. Pipette a measured portion into a 100 ml. Nessler tube and make up to the mark with ammonia-free water. The portion used can only be determined by trial.
7. If permanent ammonia standards (45) are available, proceed to Step 8. If not, make up temporary standards by adding 0.2, 0.4, 0.6, 0.8, 1.0, 1.7, 2.0, 2.5, and 3.0 ml. of standard ammonium chloride (46) to 100 ml. Nessler tubes and making up to the mark with ammonia-free water.
8. Add 2 ml. of Nessler reagent to the sample and to each temporary standard.
9. After standing 10 minutes, compare the colors and record the standard having a color nearest that of the sample.

Calculations

$$\frac{\text{ml. standard NH}_4\text{Cl} \times 2000}{\text{ml. portion used in Step 6} \times \text{ml. of sample}} = \text{p.p.m.}$$

albuminoid nitrogen as N.

Organic nitrogen, Kjeldahl method

Reagents. Section II, Nos. (2), (44), (47), (55), (74), (45), (46).

1. Measure 50 ml. of the well mixed sample and 50 ml. of distilled water into a 500 ml. Kjeldahl flask.
2. Connect to the distillation apparatus and boil until the distillate is free from ammonia as shown by adding a few drops of Nessler reagent (47) to a small portion of the distillate. The volume will be reduced about one half.

3. Cool the distillate and add 1 ml. of 10 per cent copper sulphate (74) and 10 ml. of concentrated sulphuric acid.
4. Digest in the fume hood until white fumes of sulphuric acid are obtained and until the solution is clear and free from black carbon particles.
5. Cool and add about 250 ml. of ammonia-free water (44).
6. Add a few drops of phenolphthalein (2) and make alkaline with 50 per cent sodium hydroxide (55).
7. Add a few boiling chips, reconnect to the distillation apparatus, and distill until almost 200 ml. of distillate is collected in a 200 ml. volumetric flask. (The apparatus should be free from ammonia before this distillation is started.)
8. Make up the distillate to the mark with ammonia-free water and mix thoroughly.
9. Pipette a measured portion (5 ml. or more) into a 100 ml. Nessler tube and make up to the mark with ammonia-free water. The portion used will vary and must be determined by trial.
10. If permanent ammonia standards (45) are available, proceed to Step 11. If not, make up temporary standards by adding 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.7, 2.0, 2.5 and 3.0 ml. of standard ammonium chloride (46) to 100 ml. Nessler tubes making up to the mark with ammonia-free water.
11. Add 2 ml. of Nessler reagent (47) to the sample and to each temporary standard.
12. After standing 10 minutes, compare the colors and record the standard having a color nearest that of the sample.

Calculations

$$\begin{array}{r} \text{ml. of standard } \text{NH}_4\text{Cl X 2000} \\ \hline \text{ml. portion used in Step 9 X ml. of sample} \\ = \text{p.p.m. organic nitrogen as N.} \end{array}$$

Nitrite nitrogen

Reagents. Section II, Nos. (15), (50), (51), (52).

1. If the sample is colored or turbid, clarify 150 ml. by adding 2 ml. of aluminum hydroxide (15). Heat to boiling and filter.
2. Place a measured portion of the filtrate (10 to 50 ml. depending upon the nitrite content) into a 100 ml. Nessler tube and make up to the mark with nitrite-free water.
3. If permanent standards are available, proceed to Step 4. If not, make up temporary standards by placing 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.7, 2.0 and 2.5 ml. of standard sodium nitrite (50) in 100 ml. Nessler tubes making up to the mark with nitrite-free water.
4. Add 2 ml. of sulphanilic acid (51) and 2 ml. of a-naphthylamine (52) to the sample and to each temporary standard.
5. Mix and allow to stand 10 minutes.
6. Compare the colors and record the standard having a color nearest that of the sample.

Calculations

$$\frac{\text{ml. standard NaNO}_2 \times 0.5}{\text{ml. portion used in Step 2}} = \text{p.p.m. nitrite nitrogen as N.}$$

Nitrate nitrogen, phenoldisulphonic acid method

Reagents. Section II, Nos. (54), (55), (56).

1. Filter 30 to 35 ml. of the sample through a filter paper.
2. Evaporate 25 ml. of the filtrate to dryness on a water bath. (Use a smaller amount if the nitrate content is high.)
3. Moisten the residue with 1 ml. of phenoldisulphonic acid (54).
4. Dilute to about 20 ml. with distilled water.
5. Add a 50 per cent solution of sodium hydroxide (55) until the maximum yellow color is developed. (Not more than 5 to 6 ml. of sodium hydroxide will be required.)

6. Filter into a 100 ml. Nessler tube, rinse the dish and paper with distilled water adding the filtered rinsings to the filtrate and make up to the mark with distilled water.
7. If permanent standards are available, proceed to Step 8. If not, make up temporary standards by placing 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 ml. of standard sodium nitrate solution (56) in 100 ml. Nessler tubes and adding 2 ml. of 50 per cent sodium hydroxide.
8. Dilute to the mark with distilled water.
9. Compare the colors and record the standard having a color nearest that of the sample.

Calculations

$$\frac{\text{ml. of standard } \text{NaNO}_3 \times 10}{\text{ml. of sample used in Step 2}} = \text{p.p.m. nitrate nitrogen as N.}$$

Chlorine demand

Reagents. Section II, Nos. (60), (75).

1. Place 100 ml. of the well mixed sewage in each of ten 8-ounce bottles.
2. Add 0.5 ml. of chlorine water (75) to the first bottle, 1.0 ml. to the second, 1.5 to the third and so on increasing by 0.5 ml. until all 10 bottles have been treated.
3. Shake each bottle gently and allow to stand for 30 minutes.
4. Add a crystal of potassium iodide and 1 ml. of starch solution (60) to each bottle and mix. Record the ml. of chlorine water in the first bottle which shows a blue color.

Calculations

$$\text{Ml. of chlorine water in first bottle to show a blue color} \times 5 = \text{p.p.m. chlorine demand.}$$

Chlorine residual, o-tolidine method

Reagents. Section II, Nos. (66), (67).

1. Place 50 ml. of sample in a Nessler tube.
2. Add 1 ml. of o-tolidine solution (66).

3. A yellow color indicates the presence of residual chlorine.
4. For a quantitative estimation, allow the sample to stand for 5 minutes in a dark place and compare the color with permanent standards (67). Record the standard having a color nearest that of the sample.

Residual chlorine, starch-iodide method

Reagents. Section II, Nos. (60), (68).

1. Place 200 ml. of the sample in an Erlenmeyer flask.
2. Add about 1 gram of potassium iodide crystals and 1 ml. of concentrated hydrochloric acid.
3. Add 1 ml. of starch solution (60). A blue color indicates the presence of chlorine.
4. For a quantitative estimation, titrate the solution with 0.001 N sodium thiosulphate solution (68) until the blue color just disappears. Record the ml. of thiosulphate used.

Calculations

$$\text{ml. of } 0.001 \text{ N sodium thiosulphate} \times 0.1773 \\ = \text{p.p.m. residual chlorine.}$$

Chlorides

Reagents. Section II, Nos. (13), (14).

1. If the sample contains hydrogen sulphide, acidify a 50 ml. portion in an evaporating dish with sulphuric acid. Boil, cool, and neutralize by adding a saturated solution of sodium carbonate drop by drop until no more effervescence.
2. If hydrogen sulphide is not present, omit Step 1. Pipette 50 ml. of the sample into an evaporating dish.
3. Place 50 ml. of distilled water in a second dish for a comparison of color.
4. Add 1 ml. of potassium chromate indicator (13) to sample prepared by either Step 1 or 2 and to the distilled water.

5. Add standard silver nitrate (14) a few drops at a time from a burette to the sample until the first permanent reddish color is obtained. Record the ml. of silver nitrate used.
6. If more than 7 or 8 ml. of silver nitrate are required, the entire procedure must be repeated using a smaller sample diluted to 50 ml. with distilled water.

Calculations

$$\frac{(\text{ml. of } \text{AgNO}_3 - 0.2) \times 500}{\text{ml. of sample}} = \text{p.p.m. chloride radical (Cl).}$$

Fats (Grease)

Reagents. Section II, Nos. (4), (76).

1. Place 500 ml. of the sample in an evaporating dish and evaporate over a water bath until the volume is reduced to about 50 ml.
2. Scrape the solids from the sides into the liquid with a glass rod, add a few drops of methyl orange (4) and 1 N hydrochloric acid (76) until the solution is red.
3. Evaporate to dryness on the water bath and dry for 30 minutes in the 103°C oven.
4. Weigh a 150 ml. Soxhlett flask which has been previously dried and cooled.
5. Bring about 50 ml. of ether to boiling on a steam bath or water bath from which the flame has been removed.
6. Pour the ether over the solids in the evaporating dish and rub in well with stirring rod.
7. Decant the ether through a dry filter into the Soxhlett flask.
8. Repeat the extractions twice using 20 ml. portions of ether.
9. Evaporate the ether on the bath, dry the flask at 103°C and cool in a desiccator.
10. Weigh the flask and extract.

Calculations

$$\text{Difference in weight (grams)} \times 2000 = \text{p.p.m. fat.}$$

Hydrogen sulphide H₂S)

Reagents. Section II, Nos. (59), (60), (69).

1. Syphon 500 ml. of the sample into a graduated cylinder.
2. Pipette 10 ml. of 0.025 N iodine solution (69) into each of two Erlenmeyer flasks.
3. Add about 1 gram of potassium iodide to each.
4. To one flask add 200 ml. of distilled water.
5. Into the other flask syphon from the graduate 200 ml. of the sample.
6. Titrate both the distilled water blank and the sample with 0.025 N sodium thiosulphate (59) using starch as an indicator (60) near the end of the titration.

Record the ml. of thiosulphate used in each case.

Calculations

Let S = 10 - ml. of sodium thiosulphate used for sample.

And D = 10 - ml. of sodium thiosulphate used for distilled water.

$$\frac{(S - D) \times 426}{\text{ml. of sample}} = \text{p.p.m. hydrogen sulphide.}$$

Moisture of sewage sludge

1. Ignite, cool in a desiccator and weigh a clean evaporating dish of about 50 ml. capacity.
2. Mix the sludge thoroughly and pour approximately 25 ml. into the dish.
3. Reweigh immediately avoiding delay as the sludge changes in weight rapidly.
4. Evaporate on the water bath until dry.
5. Place in the 103°C oven for at least one hour, cool in the desiccator and weigh.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 100}{\text{Weight of wet sludge (grams)}} = \text{per cent moisture.}$$

Note

The weighings need not be carried closer than to the nearest 0.01 gram.

Example

Wt. of dish and wet sludge	58.12	grams
Wt. of dish	33.75	"
Wt. of wet sludge	24.37	"
Wt. of dish and wet sludge	58.12	grams
Wt. of dish and dry sludge	35.24	"
Loss in weight	22.88	"

$$\text{Moisture} = \frac{22.88 \times 100}{24.37} = 93.9 \text{ per cent.}$$

$$\text{Solids, dry} = 100 - 93.9 = 6.1 \text{ per cent.}$$

Volatile matter of sewage sludge

1. Ignite the dish containing the dry solids from the moisture determination at a low red heat in the furnace or over a burner until no black residue remains.
2. Cool, moisten with distilled water and dry in the 103°C oven for one hour.
3. Cool in the desiccator and weigh.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 100}{\text{Weight of dry solids (grams)}} = \text{per cent volatile matter.}$$

Example

Wt. of dish and dry solids	35.24	grams
Wt. of dish	33.75	"
Wt. of dry solids	1.49	"
Wt. of dish and dry solids	35.24	grams
Wt. of dish and ash	34.22	"
Loss in weight	1.02	"

$$\text{Volatile matter} = \frac{1.02 \times 100}{1.49} = 68.5 \text{ per cent.}$$

Specific gravity of sewage sludge

1. Weigh an empty wide-mouth glass-stoppered bottle or flask of about 8-ounce or more capacity to the nearest 0.1 gram.
2. Fill to overflowing with distilled water, insert the stopper, dry with a cloth and weigh.

3. Completely empty the bottle, fill to overflowing with the well mixed sludge and insert the stopper.
4. Wash the sludge from the outside of the bottle, dry with a cloth and weigh.

Calculations

$$\frac{\text{Weight of the sludge (grams)}}{\text{Weight of distilled water (grams)}} = \text{specific gravity of sludge.}$$

Hydrogen ion concentration (pH) of sewage sludge, colorimetric method

1. Place about 20 ml. of the sludge in a 100 ml. graduate or a similar tall cylinder and dilute to about five times its volume with a good quality distilled water.
2. Mix well and allow to settle.
3. Place 10 ml. of the supernatent liquor into each of the two or three tubes provided with the pH apparatus.
4. To one tube add the designated quantity of indicator.
5. Place the tubes in the comparator in such a manner that the color standards are opposite the tubes not containing the indicator. The color comparison must be made by looking through the same thickness of liquid having the same color and turbidity as the sample.
6. Compare the colors and select the standard having a color nearest that of the sample.

Hydrogen ion concentration (pH), quinhydrone electro-metric method

Specific directions for this method accompany the apparatus when shipped from the manufacturer. These directions must be followed explicitly if good results are to be obtained. Most of the poor results reported with this apparatus are due to contamination of the electrodes, bridges, etc.

When used with sewage sludge, the sludge need not be diluted as is necessary with colorimetric equipment.

Fats (Grease), sewage sludge

Reagents. Section II, Nos. (4), (76).

1. Weigh a clean, dry evaporating dish.
2. Mix the sludge sample thoroughly and pour about 25 ml. into the weighed dish.
3. Reweigh rapidly and record the weight of sludge used.
4. Add a few drops of methyl orange (4) and then add 1 N hydrochloric acid (76) until the supernatent liquid is red.
5. Evaporate to dryness on a water bath and dry for 30 minutes in the 103°C oven.
6. Dry, cool and weigh a clean 150 ml. Soxhlett flask.
7. Bring about 50 ml. of ether to boiling on a water bath from which the flame has been removed.
8. Pour the ether over the solids in the dish and rub in well with stirring rod.
9. Decant the ether through a dry filter paper into the Soxhlett flask.
10. Repeat the extraction three times using about 25 ml. portions of ether each time.
11. Evaporate the ether on the bath with flame removed, dry the flask at 103°C, and cool in a desiccator.
12. Weigh the flask and extract.

Calculations

$$\frac{\text{Gain in weight (grams)} \times 100}{\text{Weight of sample (grams)}} = \text{per cent fat (grease).}$$

Fertilizer value of sewage sludge

The fertilizer series includes the determination of humus (organic matter), phosphoric acid, nitrogen, and potash. The sample should be carefully taken to thoroughly represent the sludge. It is customary to report fertilizer values on a

dry basis and, therefore, it is necessary to precede them by a moisture determination, if it is desired to know their significance in relation to the dry sludge. It is also necessary to grind the sludge (which can only be done on a dried sample) in order to insure ready digestion in the phosphoric acid and nitrogen determinations and to make portions of the sample used representative of the entire sample.

Moisture

1. Weigh an evaporating dish, add about 100 grams or more of the sludge and weigh again. The difference in weights will be the weight of the sample.
2. Evaporate over a water bath, dry in the oven at 103°C for 2 hours, cool in a desiccator and weigh.

Note

These weighings need be carried only to the nearest 0.1 gram.

Calculations

$$\frac{\text{Loss in weight (grams)} \times 100}{\text{Weight of sample (grams)}} = \text{per cent moisture.}$$

Sludge preparation

Grind the entire residue from the above moisture determination to a fine state and preserve in a tightly stoppered bottle. If the quantity of sample is too large to be preserved, it may be reduced in size as follows: Place the entire ground sample in a pile, divide it into quarters and retain opposite quarters. Repeat the quartering until the remaining sample is of the desired size. The grinding may be omitted if humus is the only determination to be made or if the sample is a commercial sludge fertilizer which has already been dried and ground.

Humus (Organic matter)

Reagents. Section II, Nos. (17), (18)

1. Ignite, cool, and weigh an evaporating dish.

2. Place about 2 grams of the prepared sample in the dish and reweigh.
3. Place in a 103°C oven for 2 hours or until the weight is constant, cool in a desiccator and weigh.
4. Ignite at a cherry red heat (about 900°C) for 1 hour.
5. Cool in desiccator and weigh.

Note

In order to allow for an appreciable loss of CO₂ in the above ignition due to the decomposition of calcium carbonate, it is necessary to determine the amount of the latter compound as follows.

This does not take into account the possible decomposition of other inorganic compounds which may be present in lesser amounts in the sludge.

6. Carefully add about 5 ml. of concentrated hydrochloric acid to the ash in the dish, warm gently, add about 50 ml. of distilled water and warm again.
7. Rinse into a beaker, add 10 ml. of 10 per cent ammonium chloride (17) and make alkaline to litmus with concentrated ammonium hydroxide.
8. Cover with a watch glass, warm gently for a few minutes and filter off the iron and aluminum hydroxides, rinsing the beaker and paper with small portions of distilled water and adding the filtered rinsings to the filtrate.
9. Add slowly, with constant stirring, about 10 ml. of saturated ammonium oxalate (18) and set the beaker in a warm place for 30 minutes.
10. Filter the precipitate onto a quantitative filter paper and wash well with hot distilled water.
11. Ignite, cool, and weigh a clean crucible.
12. Place the paper and precipitate in the crucible, dry, and ignite at a cherry red heat in the muffle furnace or over a blast lamp.
13. Cool in the desiccator and weigh. Repeat the ignition until the weight is constant.

Calculations

Weight in Step 2 - weight of dish = weight of dry sample.

$$\frac{(\text{Weight in Step 3} - \text{weight in Step 5}) \times 100}{\text{weight of dry sample}}$$

= per cent volatile matter.

Weight of crucible and residue in Step 13 - weight of crucible in Step 11 = weight of CaO.

$$\frac{\text{Weight of CaO} \times 178.5}{\text{Weight of dry sample}} = \text{per cent CaCO}_3 \text{ in sample.}$$

Per cent volatile matter - (0.44 X per cent CaCO₃)
= per cent humus in sample.

Phosphoric acid (P₂O₅)

Reagents. Section II, Nos. (2), (77), (78), (79).

1. Dry, cool, and weigh a crucible and add about 2 grams of the sample prepared as given under "Sludge preparation", pages 69 and 70.
2. Dry in the 103°C oven for 2 hours or until constant weight, cool in a desiccator and weigh.
3. Transfer the dried sample to a Kjeldahl flask and add about 30 ml. of concentrated sulphuric acid and 10 grams of anhydrous sodium sulphate.
4. Boil in the fume hood until the organic matter is destroyed. Cool, rinse into a 200 ml. volumetric flask, make up to the mark with distilled water and mix thoroughly. The distilled water should be added carefully with constant mixing.
5. Filter a portion and pipette 50 ml. of the filtrate into a beaker.
6. Add 5 ml. of concentrated nitric acid and then add concentrated ammonium hydroxide until the precipitate which forms, dissolves very slowly on stirring.
7. Dilute to about 100 ml. and heat in a water bath to 55 to 60°C.
8. Add 20 to 25 ml. of freshly filtered molybdate solution (77) and allow the mixture to remain in the bath with occasional stirring for 30 minutes.

9. Decant the solution through a filter paper and wash the precipitate in the beaker twice with about 25 ml. portions of distilled water, filtering each washing through the same paper.
10. Transfer the entire precipitate to the paper and wash with distilled water until a portion of the filtrate gives a pink color upon the addition of phenolphthalein (2) and a drop of sodium hydroxide (78).
11. Transfer the precipitate and filter to a beaker and dissolve the precipitate in a small excess of 0.3238 N sodium hydroxide (78), recording the ml. of hydroxide used.
12. Add a few drops of phenolphthalein and titrate the excess hydroxide with 0.3238 N hydrochloric acid (79), recording the ml. of acid used.

Calculations

$$\frac{(\text{ml. } 0.3238 \text{ N NaOH} - \text{ml. } 0.3238 \text{ N HCl}) \times 0.4}{\text{weight (grams) of dry sample used in Step 2}} \\ = \text{per cent P}_2\text{O}_5.$$

Total nitrogen

Reagents. Section II, Nos. (44), (55), (80), (81), (82).

1. Dry, cool and weigh a crucible. Add about 1 gram of the sample prepared as directed under "Sludge preparation", pages 69 and 70.
2. Dry in the 103°C over for 2 hours or until constant weight, cool in a desiccator, and weigh.
3. Transfer the dried sample to a Kjeldahl flask, add 30 to 35 ml. of salicylic acid mixture (80) and shake until well mixed.
4. Allow to stand 30 minutes with frequent shaking.
5. Add 5 grams of sodium thiosulphate crystals and heat gently for 5 minutes in a hood.
6. Cool and add 10 grams of potassium sulphate crystals.
7. Heat gently in the hood until foaming ceases and then boil until a clear straw-colored liquor is obtained. (Usually not less than 2 hours.)

8. Cool, dilute with about 200 ml. of ammonia-free water (44) and add a few boiling chips.
9. Add sufficient sodium hydroxide (55) to make the solution strongly alkaline to phenolphthalein.
10. Steam out the distillation apparatus until free from ammonia and connect the Kjeldahl flask.
11. Place 50 ml. of 4 per cent boric acid (81) in an Erlenmeyer flask and place in such a manner that the tip of the condenser extends just below the solution in the flask.
12. Distill about 150 ml. of the mixture into the boric acid.
13. Titrate the boric acid mixture with standard hydrochloric acid (82) using methyl orange as an indicator and record the ml. of acid used.

Calculations

$$\frac{\text{ml. of } 0.5 \text{ N HCl} \times 0.7}{\text{weight of dried sample in Step 2}} = \text{per cent ni-}$$

rogen as N.

$$\text{Per cent nitrogen as N} \times 1.217 = \text{per cent nitro-}$$

gen as NH₃.

Potash

Reagents. Section II, Nos. (22), (23), (24), (25).

1. Dry, cool and weigh an evaporating dish, add about 10 grams of the sample prepared as directed under "Sludge preparation", pages 69 and 70. Dry in the 103°C oven, cool in a desiccator, and reweigh.
2. Saturate the sample with concentrated sulphuric acid and ignite in a muffle furnace or over a burner at low red heat until the black carbon is completely burned.
3. Cool, add 5 ml. of concentrated hydrochloric acid and warm to dissolve the acid-soluble material.
4. Add about 50 ml. of distilled water and filter into a 500 ml. volumetric flask, rinsing the dish and paper with several portions of distilled water and adding the filtered rinsings to the filtrate.

5. Make up to the mark with distilled water and mix thoroughly.
6. Pipette 200 ml. of the solution into a beaker, heat to boiling and add drop by drop, with constant stirring, a slight excess of barium chloride solution (22).
7. Without filtering, add a slight excess of barium hydroxide solution (23) in the same manner.
8. Filter while hot and rinse the beaker and paper with four or five small portions of distilled water or until free from chlorides, adding the filtered rinsings to the filtrate. (To test for chlorides collect about 1 ml. of the filtrate in a test tube and add a few drops of silver nitrate. A white precipitate shows chlorides. The tested portion must be discarded.)
9. Add 1 ml. of concentrated ammonium hydroxide to the filtrate and a slight excess of ammonium carbonate.
10. Heat and add about 0.75 grams of ammonium oxalate.
11. Filter and wash free from chlorides as in Step 8.
12. Evaporate the filtrate to dryness in a platinum dish.
13. Ignite carefully over a free flame below red heat until no more fumes are evolved.
14. Dissolve the residue in hot distilled water, filter and rinse the dish and paper with distilled water.
15. Acidify the filtrate with a few drops of hydrochloric acid and add about 2 ml. of platinic chloride (24).
16. Evaporate on a water bath to a thick paste and treat the residue with 80 per cent alcohol (25).
17. Filter onto a previously prepared and weighed Gooch crucible (see Steps 1 to 4 inc. page 3) and wash with 80 per cent alcohol until the filtrate is colorless. Be sure the entire precipitate is transferred to the crucible, rinsing only with 80 per cent alcohol.

18. Dry the crucible at 103°C for 30 minutes and weigh.

Calculations

Difference in weight of crucible (grams) X 0.484
= grams of K₂O in the sample.

$$\frac{\text{Grams of K}_2\text{O} \times 100}{\text{Weight of sample (grams)}} = \text{per cent K}_2\text{O in sludge.}$$

Sewage Gas Analysis

The analysis of gas produced by the digestion of sewage sludge should include the determination of carbon dioxide and methane and a calculation of the B.t.u. value. The determination of hydrogen may be included, but the other gases, such as oxygen, carbon monoxide and nitrogen, are present in such small amounts that their determination as a routine procedure is of little value.

There are many types of apparatus on the market for the analysis of gas, but no type which is designed especially for sewage gas. Most of the apparatus are designed for a complete analysis and can be used by omitting the parts not required. The apparatus should contain a water jacketed measuring pipette, an explosion or burning pipette (preferably the latter) and a pipette for carbon dioxide.

Carbon dioxide

Reagents. Section II, No. (83).

1. Waste a portion of the gas to the air in order to clear the lines and to obtain a representative sample. If the gas is not piped to the laboratory, a sample may be collected at any convenient place on the gas domes or from the lines to the burners. It should be collected in a flat rubber gas bag capable of holding about 1 liter.
2. Raise the leveling tube and fill the measuring pipette completely with the liquid. (Mercury is preferred.)

3. Attach the bag or pipe line and draw about 100 ml. of the gas into the pipette by lowering the leveling tube.
4. Close the stopcock connecting the gas bag or gas line and carefully measure the volume of gas in the pipette. (The volume of gas in the pipette should always be measured by holding the level of the liquid in the leveling tube at the same elevation as that in the pipette.)
5. Open the connection to the potassium hydroxide (83) pipette and pass the gas into that pipette, allowing it to remain in contact with the solution for some time.
6. By lowering the leveling tube, bring back the entire volume of remaining gas into the measuring pipette.
7. Close the connection and measure the volume as before.
8. Repeat Steps 5, 6 and 7 until there is no further gas absorbed from contact with the potassium hydroxide solution.

Note

The apparatus must be free from leaks. Keep the glass stopcocks well greased.

Calculations

$$\frac{\text{ml. of gas absorbed} \times 100}{\text{ml. of gas used}} = \text{per cent carbon dioxide.}$$

Hydrogen, methane and B.t.u.

1. Record the volume of gas remaining in the measuring pipette from the carbon dioxide determination and call it the "gas residue."
2. Discard all but 10 ml. of this gas.
3. Lower the leveling tube and open the stopcock to the air, drawing in air until the volume is about 95 to 100 ml.
4. Measure the volume of the mixture accurately.
5. Allow the gases to mix thoroughly.
6. Close the stopcock and check on the leveling tube connection and explode or burn the gas in the pipette.

7. Allow the gas to cool to room temperature, open the check on the leveling tube and read the volume of gas remaining in the pipette.
8. Determine the amount of carbon dioxide produced by passing the gases into the potassium hydroxide pipette several times until no further loss in volume is obtained.
9. Again read the volume of gas in the measuring pipette.

Calculations

$[(\text{ml. of mixture in Step 4} - \text{ml. read in Step 7}) \\ \times \text{ml. gas residue } X 10] \div \text{ml. of sample} = \text{per cent hydrogen.}$

$[\text{ml. gas residue } X (\text{ml. absorbed in Steps 8 and 9}) X 10] \div \text{ml. of sample} = \text{per cent methane.}$

$(\text{Per cent methane } X 10.03) + (\text{per cent hydrogen } X 3.29) = \text{B.t.u. per cubic foot (high heat value, } 62^{\circ}\text{F and 760 mm).}$

$(\text{Per cent methane } X 9.13) + (\text{per cent hydrogen } X 2.81) = \text{B.t.u. per cubic foot (low heat value, } 62^{\circ}\text{F and 760 mm)}$

Part C. Polluted Water Analysis

Note. Numbers inclosed in parentheses, thus (3) refer to numbered reagents and solutions in Section II.

Dissolved oxygen, Winkler method

Reagents. Section II, Nos. (57), (58), (59), (60).
Note

The Winkler method for the determination of dissolved oxygen can be used in the majority of

cases. If the water is high in nitrates or organic matter, as is sometimes the case in badly polluted waters, the Rideal-Stewart modification will give more accurate results. The effect of nitrates on the Winkler method, however, can be minimized by carefully following the directions given below.

1. Collect the sample in an 8-ounce glass-stoppered bottle being very careful to avoid contact of the sample with air. (See "Sampling for dissolved oxygen", page 174.) The bottle should be completely filled.
2. Immediately after collection, add 1 ml. of manganese sulphate solution (57) by means of a pipette, dipping the end of the pipette just below the surface of the water in the bottle.
3. Add 1 ml. of alkaline potassium iodide (58) in a similar manner.
4. Insert the stopper and mix by inverting the bottle several times.
5. Allow the precipitate to settle halfway and mix again.
6. Again allow the precipitate to settle halfway.
7. Add 1 ml. of concentrated sulphuric acid, insert the stopper at once and mix as before.
8. Allow the solution to stand at least 5 minutes. (The solution can safely stand several hours in this condition.)
9. Rapidly withdraw 100 ml. of the solution into an Erlenmeyer flask and titrate with 0.025 N sodium thiosulphate solution (59) until the yellow color almost disappears.
10. Add about 1 ml. of starch solution (60) and continue the titration until the blue color just disappears. Record the ml. of thiosulphate used. Disregard any return of the blue color.

Calculations

$$\text{Ml. of } 0.025 \text{ N thiosulphate} \times 2 = \text{p.p.m. dissolved oxygen.}$$

Dissolved Oxygen, Rideal-Stewart modification

Reagents. Section II, Nos. (57), (58), (59), (60), (61), (62).

1. Collect the sample in an 8-ounce, glass-stoppered bottle being careful to avoid contact of the sample with air. (See "Sampling for dissolved oxygen", page 174.) The bottle should be completely filled.
2. Immediately after collecting, add 0.7 ml. of concentrated sulphuric acid and 1 ml. of potassium permanganate (61) by means of pipette dipping just below the surface of the water in the bottle.
3. Insert the stopper and mix by inverting the bottle several times.
4. If the color does not last for 30 minutes, add 1 ml. more of the potassium permanganate. If this is not sufficient, use a stronger solution.
5. After 20 minutes, add 1 ml. of potassium oxalate (62), insert the stopper and mix.
6. After the color has disappeared, add 1 ml. of manganeseous sulphate (57) and 3 ml. of alkaline potassium iodide (58), insert the stopper and mix.
7. Allow the precipitate to settle halfway and mix again.
8. Again allow the precipitate to settle halfway.
9. Add 1 ml. of concentrated sulphuric acid, insert the stopper and mix immediately. Do not allow the bottle to stand open after the addition of the acid.
10. Allow the solution to stand at least 5 minutes. (The solution may stand several hours in this condition.)
11. Rapidly withdraw 100 ml. of the solution into an Erlenmeyer flask and titrate with 0.025 N sodium thiosulphate (59) until the yellow color almost disappears.
12. Add 1 ml. of starch solution (60) and continue the titration with thiosulphate until the blue

color just disappears. Record the ml. of thiosulphate used. Disregard any return of the blue color.

Calculations

Ml. of sodium thiosulphate X 2 = p.p.m. dissolved oxygen.

Biochemical oxygen demand

Case 1

If the water is not badly polluted, the sample may contain sufficient dissolved oxygen to satisfy the 5-day oxygen demand.

1. Take two samples according to the method given for "Sampling for dissolved oxygen", page 174. Use 8-ounce glass-stoppered bottles.
2. Make a dissolved oxygen determination on one sample immediately.
3. Incubate the other sample at 20°C for 5 days.
4. Make a dissolved oxygen determination on the incubated sample.

Calculations

P.p.m. of D.O. before incubation - p.p.m. of D.O. after incubation = p.p.m. 5-day B.O.D.

Case 2

If the stream is badly polluted, the sample will require dilution prior to incubation.

1. Take two or more samples according to the method given for "Sampling for dissolved oxygen", page 174.
2. Syphon 750 ml. of diluting water (71) into a liter graduate.
3. Mix the sample and carefully syphon 250 ml. of the sample into the diluting water contained in the graduate.
4. Mix by means of a plunger type stirring rod, being as careful as possible to prevent aeration. This is a 25 per cent dilution.
5. Fill two 8-ounce bottles with the dilution by means of a syphon, insert the stoppers and seal one bottle with a water seal.

6. Now remove by means of the siphon all but 400 ml. of the 25 per cent dilution remaining in the graduate.
7. Add diluting water to the liter mark, mix as before and fill two more bottles with this dilution. This is a 10 per cent dilution.
8. Insert the stoppers and seal one bottle with a water seal.
9. Set the two sealed bottles (one from each dilution) in the 20°C incubator for 5 days.
10. Make a dissolved oxygen determination immediately on the other two bottles.
11. After 5 days make a dissolved oxygen determination on the incubated samples.

Calculations

$$\frac{(\text{p.p.m. of D.O. before incubation} - \text{p.p.m. of D.O. after incubation}) \times 100}{\text{per cent dilution}}$$

= p.p.m. 5-day B.O.D.

Cyanides, qualitative test

Reagents. Section II, Nos. (84), (85).

1. Place 1 ml. of phenolphthalin (not phenolphthalein) solution (84) and 0.5 ml. of copper sulphate solution (85) in each of two test tubes.
2. To one add 15 ml. of freshly boiled and cooled distilled water.
3. To the other add 15 ml. of the sample.
4. A pink color, which develops immediately, shows the presence of cyanides. This test is sensitive to about 0.4 p.p.m. cyanide (CN).

Note

On standing the pink color may develop even in the distilled water due to the oxidation of the phenolphthalin by the dissolved oxygen. The test is not entirely specific for cyanides as chlorine and some other oxidizing agents give the same test.

Combined Acids and Iron in Spent Pickling Liquors
and Similar Wastes

Reagents. Section II, Nos. (86), (95), (16).

1. Pipette 10 ml. of the waste into a 100 ml. volumetric flask and make up to the mark with distilled water.
2. Mix thoroughly and pipette 10 ml. (or a larger portion depending upon the concentration of the waste) into a 250 ml. beaker and dilute with about 50 ml. of distilled water.
3. Add from a burette a measured quantity of 0.2 N sodium hydroxide (86) and record the amount used. The amount used should be more than enough to neutralize the acid and precipitate the iron.
4. Heat gently for a few minutes and filter. If an excess of sodium hydroxide has been added, the filtrate will give a pink color with a few drops of phenolphthalein.
5. Rinse the beaker and wash the paper and precipitate with small portions of hot water.
6. Add a few drops of phenolphthalein to the filtrate and washings and titrate with 0.1 N sulphuric acid (95) until the pink color just disappears. Record the ml. of acid used.

Calculations

$$\frac{\text{ml. } 0.2 \text{ N NaOH} - (0.5 \times \text{ml. } 0.1 \text{ N H}_2\text{SO}_4) \times 98.1}{\text{ml. of portion of diluted sample used in Step 2}}$$

= grams per liter of combined acid and iron expressed as H_2SO_4 .

7. Pipette 10 ml. of the diluted waste from Step 1 into a beaker and add about 40 ml. of distilled water and 5 ml. of concentrated hydrochloric acid.
8. Add about 10 ml. of bromine water (16), cover with a watch glass and boil for about 10 minutes.
9. Make distinctly alkaline to litmus with concentrated ammonium hydroxide and boil gently for 10 minutes.
10. Ignite, cool and weigh a crucible.
11. Filter the precipitate onto a quantitative filter paper and rinse and wash with hot distilled water.

12. Place the paper in the crucible, ignite, cool in a desiccator and weigh.

Calculations

$$\frac{\text{Gain in weight (grams)} \times 19000}{\text{ml. of portion of diluted sample used}} = \text{grams}$$

FeSO_4 per liter.

(Grams combined acid and iron per liter) - (grams FeSO_4 per liter \times 0.645) = grams H_2SO_4 per liter.

Grams FeSO_4 per liter \times 0.368 = grams Fe per liter.

Iron, volumetric method

Reagents. Section II, No. (94).

Note

This method is adapted to the determination of iron in metal pickling liquors and other ferric and ferrous iron solutions.

1. Use an appropriate amount of the sample depending upon the iron content. The sample should not contain more than 0.15 grams Fe. Usually about 1 ml. of the concentrated iron solutions is sufficient. In order to measure this amount more accurately than is possible with a 1 ml. pipette, pipette 10 ml. of the sample into a 100 ml. volumetric flask, dilute to the mark, mix thoroughly and use a 10 ml. portion.
2. Measure the sample into a casserole and carefully add 4 ml. of concentrated sulphuric acid.
3. Evaporate over a free flame, keeping the casserole in constant motion, until the white fumes of sulphuric acid appear.
4. Cool and carefully add about 50 ml. of distilled water.
5. Rinse the solution into a 250 ml. Erlenmeyer flask, keeping the volume below 100 ml.
6. Add two grams of iron-free zinc (granular) and carefully warm until the zinc is dissolved.
7. Cool and titrate at once with 0.1 N potassium permanganate (94) to the first permanent pink color, recording the ml. of permanganate used.

Note

If iron-free zinc is not available, carry a sample of distilled water through the same procedure. The ml. of permanganate required for the blank represents the iron in the zinc used and must be subtracted from the ml. of permanganate used for the sample.

Calculations

$$\frac{\text{ml. of } 0.1 \text{ N } \text{KMnO}_4 \times 0.005584}{\text{ml. of sample used}} = \text{grams Fe per ml.}$$

$$\text{Grams Fe per ml.} \times 2.905 = \text{grams } \text{FeCl}_3 \text{ per ml.}$$

$$\text{Grams Fe per ml.} \times 2.72 = \text{grams } \text{FeSO}_4 \text{ per ml.}$$

$$\frac{\text{Grams per ml.} \times 100}{\text{Specific gravity}} = \text{per cent by weight.}$$

Alkalies

Reagents. Section II, Nos. (2), (3), (95), (4).

1. Measure an appropriate amount of the sample (100 ml. or a smaller amount diluted to 100 ml. with distilled water) into an Erlenmeyer flask.
2. Add 3 drops of phenolphthalein (2).
3. If the solution becomes pink, hydroxide or carbonate alkalinity is present. Add 0.1 N sulphuric acid (95) (use 0.02 N sulphuric acid (3) if the alkalinity is slight) drop by drop from a burette until the pink color just disappears. Record the ml. of acid used.
4. Add 3 drops of methyl orange (4) and again titrate with the 0.1 N sulphuric acid to the first slight change in color. Record the ml. of acid used.

Calculations

Let P = ml. 0.1 N H_2SO_4 used for the phenolphthalein reaction.

Let T = the sum of the ml. used for the phenolphthalein and methyl orange titrations.

1. When P = T

$$\frac{P \times 1.7}{\text{ml. of sample}} = \text{grams hydroxide (OH) per liter.}$$

2. When P is greater than 1/2 T.

$$\frac{(2P - T) \times 1.7}{\text{ml. of sample}} = \text{grams hydroxide (OH) per liter.}$$

$$\frac{2(T - P) \times 3.0}{\text{ml. of sample}} = \text{grams carbonate (CO}_3\text{) per liter.}$$

3. When P = 1/2 T

$$\frac{T \times 3.0}{\text{ml. of sample}} = \text{grams carbonate (CO}_3\text{) per liter.}$$

4. When P is greater than 1/2 T

$$\frac{2P \times 3.0}{\text{ml. of sample}} = \text{grams carbonate (CO}_3\text{) per liter.}$$

$$\frac{(T - 2P) \times 6.1}{\text{ml. of sample}} = \text{grams bicarbonate (HCO}_3\text{) per liter.}$$

5. When P = 0

$$\frac{T \times 6.1}{\text{ml. of sample}} = \text{grams bicarbonate (HCO}_3\text{) per liter.}$$

Note

If 0.02 N H₂SO₄ was used, the results of the above calculations must be divided by 5.0.

Phenols, Baylis modification of Gibb's method

Reagents. Section II, Nos. (98), (87), (88), (100), (55), (101).

Note

This method is designed for water, sewage or wastes having a phenol content up to 50 p.p.m.

For wastes (ammonia still liquors, etc.) having a phenol content greater than 50 p.p.m., use the bromine method which follows this procedure.

Case I

For sewage or waste containing from 0.05 to 50 p.p.m. phenol.

- Pipette 200 ml. of the sample into a Kjeldahl flask and acidify with phosphoric acid (98) until just acid to methyl orange. (If the concentration

- is greater than 0.5 p.p.m., a smaller volume diluted to 200 ml. should be used.)
2. Connect the flask to the condenser of an ammonia still and distill until about 180 ml. of distillate is collected in a 200 ml. volumetric flask.
 3. Add 20 ml. of distilled water to the residue in the flask and continue the distillation until 200 ml. total distillate is collected.
 4. If necessary, filter through asbestos to remove fats.
 5. Determine the ml. of buffer solution necessary to adjust the distillate to pH 9.6 as follows: Place 50 ml. of the distillate in a Nessler tube and add 0.5 ml. of buffer solution (88). Test a 2 ml. portion of this solution for pH by adding 3 drops of thymolphthalein (87) or oleo red and comparing the color with pH standards. If pH is too low, add more buffer solution to the 50 ml. of distillate, 0.1 ml. at a time, until a pH of 9.6 is obtained. Record the ml. of buffer solution required.
 6. Make up aliquot portions of 1, 2, 5, 25 and 100 ml. of the distillate to 100 ml. in a series of Nessler tubes and add 1 ml. of copper sulphate (100) to each tube.
 7. Add a volume of buffer solution to each tube as determined by the following formula:
$$D = \text{ml. aliquot portion of distillate used.}$$
$$B = \text{ml. of buffer solution required for 50 ml. distillate.}$$
$$V = \text{ml. of buffer required to produce pH of 9.6 in the diluted aliquot portion in each tube.}$$
$$V = \left(\frac{D}{50} \right) \times B + \left(\frac{100 - D}{100} \right)$$
 8. At this point make up standards by placing 0.1, 0.3, 0.6, 1.0, 1.5, 2.0, 3.0, and 4.0 ml. of

standard phenol solution (89) into 100 ml. Nessler tubes. Add 1 ml. of copper* sulphate (100) and 1 ml. of buffer solution (88) and make up to the mark with distilled water.

9. Add 1.5 ml. of 2, 6-dibromoquinonechloroimide (90) to each standard and to the diluted aliquot distillates. Invert the tubes 3 times to mix.
10. After standing at least 2 hours, compare the colors and select the standard and aliquot having similar colors.

Calculations

$$\frac{\text{ml. of standard phenol X 2000}}{\text{ml. aliquot portion X ml. sample}} = \text{p.p.m. phenol.}$$

Case II

For polluted waters or water containing minute amounts of phenol.

1. Measure 800 ml. of the sample into a liter Kjeldahl flask, add 4 ml. of 12 N sodium hydroxide (55) and boil down to about 200 ml.
2. Proceed according to Steps 1 to 6 inclusive in Case I except that in Step 5 buffer solution (101) should be used.
3. Add a volume of buffer solution (101) to each tube as determined by the following formula:
 $D = \text{ml. aliquot portion of distillate used.}$
 $B = \text{ml. of buffer required for 50 ml. of distillate.}$

$V = \text{ml. of buffer required to produce pH of 9.6 in the diluted aliquot portion in each tube.}$

$$V = \left(\frac{D}{50} \right) X B + 5 \left(\frac{100 - D}{100} \right)$$

4. Proceed according to Steps 8 to 10 inclusive in Case I except that 5 ml. of buffer (101) is used in Step 8.

Calculations

$$\frac{\text{ml. of standard phenol X 2000}}{\text{ml. of aliquot portion X ml. of sample}} = \text{p.p.m. phenol.}$$

Phenol, bromine method

Reagents. Section II, Nos. (91), (92), (93), (60).

Note

This method is designed for wastes having phenol contents above 50 p.p.m.

1. Place 100 ml. of the sample (smaller quantity diluted to 100 ml. may be used if the phenol content is very high) into a Kjeldahl flask.
2. Add 5 ml. of 20 per cent sodium hydroxide (91) and boil off any ammonia or until the vapors have no effect on moist litmus paper.
3. Add 1 gram of lead carbonate and boil 1 minute more.
4. Add 15 grams of sodium bicarbonate and make up to about 100 ml.
5. Add boiling chips to prevent bumping and a drop of castor oil to prevent foaming.
6. Connect to the ammonia still and distill until about 90 ml. of distillate have been collected in an Erlenmeyer flask.
7. Cool and add 50 ml. of 0.1 N bromine (93) and 5 ml. of concentrated hydrochloric acid to the distillate.
8. Allow to stand in cold water for 15 minutes and add about 2 grams of potassium iodide crystals.
9. Titrate with 0.1 N sodium thiosulphate (92) using starch (60) as an indicator near the end of the titration.

Calculations

$$\frac{(50 \text{ ml. of } 0.1 \text{ N sodium thiosulphate}) \times 1560}{\text{ml. of sample used}}$$

= p.p.m. phenol.

SECTION II

REAGENTS AND STANDARD SOLUTIONS

Part I. Stock Standard Solutions

(A) Sulphuric acid

1. Place a few grams of pure anhydrous sodium carbonate in a small crucible and heat on a wire gauze over a small Bunsen flame to drive off the moisture. (Drying in a 103°C oven is preferred, if such an oven is available, in which case the drying may be done directly in the weighing bottle with the stopper removed.)
2. Cool in a desiccator and transfer the carbonate to a clean dry weighing bottle. Handle the weighing bottle with a clean dry cloth or piece of paper.
3. Weigh the bottle and contents.
4. Carefully transfer about 0.2 grams of the carbonate to a 250 ml. Erlenmeyer flask and reweigh the bottle and contents. The difference in weight is the weight of the carbonate used.
5. Weigh out a second portion into another flask in the same manner.
6. Dissolve each sample in about 80 ml. of distilled water and add 3 drops of methyl orange (4).
7. Measure by means of a small graduate about 6 ml. of concentrated sulphuric acid and transfer this and several rinsings of the graduate to a liter bottle. Dilute to approximately 1 liter with distilled water and mix.
8. Rinse a clean burette several times with about 10 ml. portions of the acid solution and then fill completely.
9. Add the acid solution from the burette to the carbonate solution in each flask with constant

mixing until the color shows the first change from the yellow. Select as the end-point the faintest trace of red in the yellow solution giving a slight orange tint. Always titrate to the same color. Record the ml. of acid used in each case.

Calculations

$$\frac{\text{Weight of } \text{Na}_2\text{CO}_3 \text{ (grams)} \times 1000}{(\text{ml. of acid used in Step 9}) \times 53} = \text{normality of acid.}$$

Note

The solution should be approximately 0.2 N.

Illustrated Example

Sample No.	Weight of weighing bottle and contents (grams)		Weight of Sodium Carbonate Used (grams)	Titration Results	
	Before removing sample	After removing sample		ml. of H_2SO_4 Used	Normality of acid solution
1	20.6971	20.2835	0.4158	37.1	0.2105
2	20.2835	19.8990	0.3843	34.5	0.2102

The values in the last column were obtained as follows:

$$\text{Sample No. 1 } \frac{0.4158 \times 1000}{37.1 \times 53} = 0.2105$$

$$\text{Sample No. 2 } \frac{0.3843 \times 1000}{34.5 \times 53} = 0.2102$$

(B) Sodium hydroxide

1. Weigh out in a beaker on a trip scale about 30 grams of pure sodium hydroxide sticks.
2. Add about 100 ml. of distilled water and let stand until the surface coating of the sticks has dissolved. (This removes any carbonate coating.)
3. Pour off the supernatent liquor and dissolve the remaining sodium hydroxide (there should be about 20 grams remaining) in boiled distilled water.

4. Transfer the solution to a liter bottle, dilute to approximately 1 liter with boiled distilled water and mix thoroughly.
5. Fill a clean burette with the sulphuric acid standard stock solution (A).
6. Pipette two portions of exactly 10 ml. each of the sodium hydroxide solution into two 250 ml. Erlenmeyer flasks, dilute to about 100 ml. and add 3 drops of phenolphthalein (4).
7. Titrate with the acid solution from the burette until the first permanent change from the yellow color is obtained. Select as the end-point the faintest trace of red in the yellow solution giving a slight orange tint. Always titrate to the same color.

Calculations

$$\frac{\text{ml. of sulphuric acid} \times \text{normality of sulphuric acid}}{\text{ml. of sodium hydroxide}}$$

$$= \text{normality of sodium hydroxide.}$$

The solution should be approximately 0.5 N.

(C) Hydrochloric acid

1. Place approximately 44 ml. of concentrated hydrochloric acid in a 1 liter bottle, make up to approximately 1 liter with distilled water and mix thoroughly.
2. Standardize the solution against sodium carbonate in the manner described for the standardization of sulphuric acid (A).

Note

It is possible to standardize the hydrochloric acid against the sodium hydroxide (B) by titration. A direct standardization, however, is preferred.

Calculations

$$\frac{\text{Wt. of sodium carbonate (grams)} \times 1000}{\text{ml. of acid used} \times 53} = \text{normality of acid.}$$

The solution should be approximately 0.5 N.

- (D) Sodium thiosulphate (stock standard solution).
1. Dissolve exactly 24.82 grams of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in distilled water and make up to 1 liter.
 2. Add 1.5 grams of ammonium carbonate and 5 ml. of chloroform as a preservative. (This solution may also be preserved by adding 0.2 per cent by weight of sodium hydroxide.)
 3. This solution is 0.1 N and is considered sufficiently accurate to be diluted for use in the ordinary dissolved oxygen determinations. As it does not keep well it should be made up new after a few weeks or restandardized. For restandardization or a more accurate standardization of the original solution use the following method.
 - a. Weigh exactly 3.250 grams of potassium biniodate ($\text{KIO}_3 \cdot \text{HIO}_3$), dissolve in distilled water, make up to 1 liter and mix thoroughly.
 - b. Dissolve about 5 grams of potassium iodide crystals in about 100 ml. of distilled water in a 250 ml. Erlenmeyer flask.
 - c. Add 10 ml. of dilute sulphuric acid (1 to 10) and exactly 25 ml. of the biniodate solution.
 - d. Titrate with the sodium thiosulphate solution using starch (60) as an indicator near the end of the titration (when a pale straw color is obtained). Record the ml. of thiosulphate used.

Calculations

$$\frac{\text{ml. of biniodate solution} \times 0.1}{\text{ml. of thiosulphate solution}} = \text{normality of sodium thiosulphate.}$$

- (E) Potassium permanganate (stock standard solution)
1. Dissolve exactly 14.210 grams of C.P. ammonium oxalate crystals, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, in distilled water and make up to 1 liter. This solution is 0.2 N.
 2. Dissolve 6.4 grams of potassium permanganate in distilled water, make up to 1 liter and mix thoroughly. Standardize as follows:

- a. Pipette 25 ml. of the ammonium oxalate solution into a 250 ml. Erlenmeyer flask and dilute to about 100 ml. with distilled water.
- b. Add 10 ml. of 1 to 3 sulphuric acid (63) and heat to 90°C.
- c. Titrate while hot with the potassium permanganate solution to the first permanent pink color, recording the ml. of permanganate used.

Calculations

$$\frac{\text{ml. of ammonium oxalate} \times 0.2}{\text{ml. of potassium permanganate}} = \text{normality of potassium permanganate.}$$

Part II. Reagents and Solutions

Note. Letters in parentheses, thus (A), refer to Stock Standard Solutions, Section II, Part I.

1. Asbestos fiber emulsion: Place 2.5 grams of finely shredded, acid-washed asbestos fiber in a liter bottle. Add 900 ml. of distilled water and shake thoroughly.
2. Phenolphthalein indicator: Dissolve 0.5 grams of phenolphthalein in 1 liter of 50 per cent alcohol. Neutralize the solution with 0.02 N sodium hydroxide (5). (To make 1 liter of 50 per cent alcohol, dilute 526 ml. of 95 per cent grain alcohol to 1 liter with boiled distilled water.)
3. Standard 0.02 N sulphuric acid: Dilute the exact quantity of stock standard sulphuric acid solution (A) as determined by the following formula to 1 liter with distilled water.

$$\frac{20}{\text{normality of stock H}_2\text{SO}_4} = \text{ml. stock H}_2\text{SO}_4 \text{ necessary to produce 1 liter of 0.02 N H}_2\text{SO}_4.$$

4. Methyl orange indicator: Dissolve 0.5 grams of methyl orange in 1 liter of distilled water.

5. Standard 0.02 N sodium hydroxide: Dilute to 1 liter with boiled distilled water, the exact quantity of stock standard sodium hydroxide (B) as determined by the following formula:

$$\frac{20}{\text{normality of stock NaOH}} = \text{ml. stock NaOH necessary to produce 1 liter of 0.02 N NaOH.}$$

6. Standard $\frac{N}{44}$ sodium hydroxide: Dilute to 1 liter with boiled distilled water the exact quantity of stock standard sodium hydroxide (B) as determined by the following formula:

$$\frac{22.73}{\text{normality of stock NaOH}} = \text{ml. of stock NaOH necessary to produce 1 liter of } \frac{N}{44} \text{ NaOH.}$$

7. Standard soap solution:

1. Make up a stock soap solution by shaking 100 grams of pure powdered castile soap with 1 liter of 80 per cent grain alcohol (25), let stand overnight and decant.
2. Prepare a standard calcium solution by dissolving 0.5 grams of pure calcium carbonate in about 5 ml. of 1 to 3 hydrochloric acid. Add about 40 ml. of boiled and cooled distilled water and add ammonium hydroxide until slightly alkaline to litmus. Make up to exactly 500 ml. with boiled and cooled distilled water. 1 ml. = 1 mg. CaCO_3 .
3. Determine the lather factor by adding the soap solution drop by drop from a burette to a 50 ml. portion of distilled water contained in an 8-ounce glass-stoppered bottle, shaking between the additions. When sufficient soap solution has been added to produce a lather which remains over the entire surface of the water for 5 minutes (bottle should be layed on its side), record the ml. of solution added. This is the lather factor.

4. Pipette 25 ml. of the standard calcium solution into a bottle, add 25 ml. boiled distilled water and titrate with soap solution as above, recording the ml. used to produce a permanent lather.
5. Adjust the soap solution so that 1 ml. equals 1 ml. of standard calcium solution. This is done by calculating the ml. of soap solution necessary to make 1 liter of required solution using the formula:

(ml. of soap solution step 4 - lather factor)
 $X 40 = \text{ml. stock soap solution required.}$

Dilute this quantity of stock solution to 1 liter with 80 per cent alcohol (25). 1 ml. = 1 mg.
 CaCO_3 .

8. Soda reagent: Dissolve 2 grams sodium hydroxide and 2.65 grams of anhydrous sodium carbonate in distilled water and make up to 1 liter.
9. Limewater: Add about 3 grams of good quality slaked lime to about 1 liter of distilled water. Shake thoroughly for some time and allow to stand until clear. Use the clear supernatent liquor.
10. Hydroxylamine hydrochloride: Dissolve 10 grams of hydroxylamine hydrochloride in 1 liter of distilled water.
11. Benzidine hydrochloride: Place 8 grams of benzidine in an agate mortar and add enough water to make a paste. Wash the paste into a liter flask, add 10 ml. of concentrated hydrochloric acid and make up to the mark. Filter if necessary.
12. Standard 0.05 N sodium hydroxide: Dilute to 1 liter with boiled distilled water the exact quantity of stock standard sodium hydroxide (B) as determined by the following formula:

$$\frac{50}{\text{normality of stock NaOH}} = \text{ml. stock NaOH necessary to produce 1 liter of 0.05 N NaOH.}$$

13. Potassium chromate indicator: Dissolve 50 grams of neutral potassium chromate in a small quantity

of distilled water. Add silver nitrate solution (14) to produce a slight red precipitate. Allow to stand overnight and filter. Make up to 1 liter.

14. Standard silver nitrate: Dissolve 2.4 grams of C.P. silver nitrate crystals in 1 liter of distilled water. This solution should be standardized against sodium chloride as follows: Dissolve 16.48 grams of C.P. fused sodium chloride in distilled water and make up to 1 liter in a volumetric flask. Mix well and pipette 100 ml. of this stock solution into a second flask. Make up to 1 liter and mix. Pipette 25 ml. of this solution into a porcelain dish and add 25 ml. of distilled water. Place 50 ml. of distilled water in another dish as a control. Add 1 ml. of potassium chromate indicator to each. Now add the silver nitrate solution from a burette drop by drop until the first permanent reddish-brown color remains after stirring.

1 ml. of the salt solution contains 1 mg. of chloride radical. The number of ml. of silver nitrate solution must be corrected for error due to variation in volume by subtracting $(0.003V + 0.02)$ where V = ml. of liquid at the end of the titration. Adjust the solution so that 2 ml. of the silver nitrate will be exactly equivalent to 1 ml. of the sodium chloride solution. Then 1.0 ml. of the silver nitrate solution will be equivalent to 0.5 mg. of the chloride radical.

15. Aluminum hydroxide: Dissolve 125 grams of pure aluminum sulphate in 1 liter of water. Add ammonium hydroxide until the precipitation is complete. Allow to settle and pour off the supernatent. Wash the precipitate in a large quantity of distilled water to remove chlorides, nitrates and ammonia.
16. Bromine water: Fill a liter bottle almost full of distilled water. In the hood, carefully pour about 10 ml. of bromine into the bottle. Stopper

and shake. Care should be used in handling bromine as the liquid or its fumes cause serious burns.

17. Ammonium chloride, 10 per cent: Dissolve 100 grams C.P. ammonium chloride in distilled water and make up to 1 liter.
18. Saturated ammonium oxalate: Place about 50 grams of C.P. ammonium oxalate in a liter bottle and fill with distilled water. Shake and let stand until almost all of the crystals are dissolved. (Use the supernatent liquor.)
19. Sulphuric acid, 2 per cent: Add 20 ml. of concentrated sulphuric acid to about 1 liter of distilled water.
20. Standard potassium permanganate (0.125 N): Dilute to 1 liter with distilled water, the exact quantity of stock standard potassium permanganate (E) as determined by the following formula:
$$\frac{125}{\text{normality of stock KMnO}_4} = \text{ml. stock KMnO}_4 \text{ necessary to produce 1 liter of 0.125 N KMnO}_4.$$
21. Disodium phosphate (10 per cent): Dissolve 100 grams of C.P. disodium phosphate (Na_2HPO_4) in distilled water and make up to 1 liter.
22. Barium chloride (10 per cent): Dissolve 100 grams of C.P. barium chloride in distilled water and make up to 1 liter.
23. Barium hydroxide (saturated): Place about 70 grams of barium hydroxide in a liter bottle. Almost fill with distilled water and shake for some time. Allow to settle and use the clear supernatent liquor.
24. Platinic chloride (10 per cent): Dissolve 10 grams platinic chloride (PtCl_4) in distilled water and make up to 100 ml.
25. Alcohol (80 per cent): To make 1 liter of 80 per cent alcohol dilute 840 ml. of 95 per cent pure grain alcohol to 1 liter with distilled water.
26. Permanent iron standards: Solution No. 1: Dissolve 0.4 grams of potassium chloroplatinate

(K_2PtCl_6) in a small amount of distilled water, add 20 ml. concentrated hydrochloric acid and dilute to 100 ml. with distilled water.

Solution No. 2: Dissolve 4.8 grams of cobaltous chloride ($CoCl_2 \cdot 6H_2O$) in a small amount of distilled water, add 20 ml. of concentrated hydrochloric acid and make up to 100 ml. with distilled water. Place the quantities of each solution as given in the following table in 100ml. Nessler tubes and dilute to the mark with distilled water.

Solution No. 1	Solution No. 2	Milligrams of iron
1.00	0.60	0.01
2.25	1.20	0.02
3.30	1.85	0.03
4.65	2.75	0.04
5.75	3.65	0.05
8.85	6.60	0.075
11.30	10.00	0.10
14.70	12.80	0.125
16.85	15.10	0.15

27. Standard iron solution: Dissolve 0.7022 grams of ferrous ammonium sulphate crystals $[FeSO_4(NH_4)_2SO_4 \cdot 6H_2O]$ in about 50 ml. of distilled water and 20 ml. of concentrated sulphuric acid. Warm and add potassium permanganate solution (28) until a slight pink color persists. Dilute to 1 liter with distilled water. 1 ml. = 0.1 mg. Fe.
28. Potassium permanganate reagent: Dissolve 6.3 grams of potassium permanganate in distilled water and make up to 1 liter.
29. Potassium thiocyanate: Dissolve 2 grams of potassium thiocyanate in distilled water and make up to 100 ml.
30. Sulphuric acid, dilute: Carefully add 100 ml. of C.P. concentrated sulphuric acid to 500 ml. of distilled water.

31. Potassium ferricyanide: Dissolve 0.5 grams of crystalline potassium ferricyanide in distilled water and make up to 100 ml. This solution does not keep well and must be freshly prepared.
32. Standard ferrous ammonium sulphate: Dissolve 0.7022 grams of crystalline ferrous ammonium sulphate $[FeSO_4(NH_4)_2SO_4 \cdot 6H_2O]$ in freshly boiled distilled water to which 10 ml. of dilute sulphuric acid (30) has been added. Dilute to 1 liter with boiled distilled water. This solution will not keep. 1 ml. = 0.1 mg. Fe.
33. Standard manganous sulphate solution: Dissolve 0.2873 grams of potassium permanganate in 100 ml. distilled water. Acidify with sulphuric acid and heat to boiling. Slowly add a dilute solution of oxalic acid until the color is just discharged. Cool and dilute to 1 liter. 1 ml. = 0.1 mg. Mn.
34. Nitric acid reagent: Add 100 ml. of concentrated nitric acid to 100 ml. of distilled water. If brown, bubble air through the solution in the hood until colorless.
35. Silver nitrate reagent. Dissolve 20 grams silver nitrate in distilled water and make up to 1 liter.
36. Standard alum solution: Dissolve 2.5 grams of aluminum sulphate crystals $[Al_2(SO_4)_3 \cdot 18H_2O]$ in boiled distilled water, add about 2 ml. of dilute sulphuric acid (30) and make up to 1 liter. This is a stock solution and must be standardized as follows:
 1. Pipette two 50 ml. portions of the well mixed solution into 250 ml. beakers.
 2. Make distinctly alkaline to litmus with ammonium hydroxide.
 3. Cover and boil gently until the odor of ammonia is slight.
 4. Filter through quantitative filter paper and wash with hot distilled water until the filtrates give no white cloudiness when treated with a drop of barium chloride (22).
 5. Ignite, cool and weigh two crucibles.

6. Place the filter papers in each of the crucibles, ignite, cool and weigh. The gain in weight is the weight of Al_2O_3 in a 50 ml. portion. The two weights should check.

The standard alum solution is made as follows: Measure a portion of the standardized stock solution, as determined by the formula below, into a liter volumetric flask. Add 2 ml. of dilute sulphuric acid (30) and dilute to the mark with boiled distilled water.

$$\frac{0.5}{\text{grams } \text{Al}_2\text{O}_3 \text{ in 50 ml. stock alum}} = \text{ml. stand-}$$

ardized stock alum solution required.

$$1 \text{ ml.} = 0.01 \text{ mg. } \text{Al}_2\text{O}_3.$$

37. Permanent alum standards: The standards prepared according to the method given in the residual alum determination may be sealed in the phosphoric acid flasks. These standards will be more permanent if a good surface water is used instead of distilled water for diluting the standard alum solution in the flasks. This water should first be stored for about 4 days and filtered.
38. Alizarin red S. (0.3 per cent): Pour 5.5 ml. of concentrated sulphuric acid into about 95 ml. of distilled water. Dissolve 0.3 grams of alizarin red S. (alizarin sodium monosulphonate) in the sulphuric acid solution.
39. Sodium bicarbonate, saturated: Mix about 100 grams of sodium bicarbonate with 1 liter of distilled water. Stir until the solution is saturated. Filter and add about 20 ml. of distilled water to the filtrate.
40. Acetic acid (50 per cent): Dilute 50 ml. of glacial acetic acid with 50 ml. of boiled distilled water.
41. Color standards: Dissolve 0.249 grams of potassium chloroplatinate (K_2PtCl_6) and 0.2 grams of crystallized cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) in a small amount of distilled water, add 20 ml. of

concentrated hydrochloric acid and dilute to 200 ml. with distilled water. Place 1, 2, 3, etc., to 10 ml. of this solution in 100 ml. Nessler tubes and dilute to the mark. These represent colors of 5, 10, 15, etc.

42. Turbidity standards 2 to 25: Place a few grams of Fuller's earth in a gallon bottle and almost fill with distilled water. Shake violently several times and allow to stand overnight. Withdraw the supernatant liquor and test the turbidity with the Jackson turbidimeter. If the turbidity is less than 50, add more earth and repeat until a turbidity is above that value. From this stock suspension make up, in liter clear-glass bottles, suspensions having turbidities of 2, 5, 10, 15, 20, and 25 by diluting an appropriate amount with distilled water. To determine the amount of stock suspension necessary to use in making up the standards, apply the following formula:

$$\frac{\text{Turbidity desired} \times 1000}{\text{Turbidity of stock suspension}} = \text{ml. stock suspension}$$

sion necessary to make 1 liter of standard.

43. Turbidity standards, Baylis turbidimeter: Make these standards in the same manner as described above. Standards having turbidities of 0.2, 0.5, 0.75, 1.0, 1.5 and 2.0 should be made.
44. Ammonia-free water: Add 2 ml. of concentrated sulphuric acid to each liter of distilled water and redistill.
45. Permanent ammonia standards: Solution No. 1: Dissolve exactly 0.4 grams potassium chloroplatinate (K_2PtCl_6) in a small amount of distilled water, add 20 ml. of concentrated hydrochloric acid and dilute to 200 ml. Solution No. 2: Dissolve exactly 1.2 grams of cobaltous chloride ($CoCl_2 \cdot 6H_2O$) in a small amount of distilled water, add 10 ml. of concentrated hydrochloric acid and make up to 100 ml.

Measure into 100 ml. Nessler tubes, the volumes of each solution as given below and dilute to the mark. Stopper tightly and keep in dark place.

ml. Solution No. 1	ml. Solution No. 2	Mg. ammonia nitrogen
2.8	0.0	0.002
4.7	0.1	0.004
5.9	0.2	0.007
7.7	0.5	0.010
9.9	1.1	0.014
12.7	2.2	0.020
15.0	3.3	0.025
17.3	4.5	0.030
19.7	7.1	0.040
20.0	10.4	0.050

46. Standard ammonium chloride: Dissolve 3.82 grams of pure ammonium chloride in 1 liter of distilled water. Mix thoroughly and dilute 10 ml. of this solution to 1 liter with ammonia-free water. 1 ml. = 0.01 mg. of N = 0.01216 NH₃.
47. Nessler's reagent: Dissolve 50 grams of potassium iodide in about 35 ml. of cold ammonia-free water. Add a saturated solution of mercuric chloride until a slight precipitate persists. Add 400 ml. of a 50 per cent solution of potassium hydroxide. Dilute to 1 liter, allow to settle and decant.
48. Alkaline potassium permanganate: Boil about 600 ml. of distilled water in a large evaporating dish for 10 minutes. Add 8 grams of potassium permanganate and stir until completely dissolved. Dissolve 180 grams of sodium hydroxide in 500 ml. of ammonia-free water (44) and let stand until any insoluble matter settles. Add 400 ml. of the clear supernatent sodium hydroxide solution to the potassium permanganate solution in the dish and make up to about 1200 ml. with ammonia-free

- water. Boil until the volume has been reduced to about 1 liter.
49. Phosphate buffer solution (pH 7.4): Dissolve 14.3 grams of mono-potassium phosphate (KH_2PO_4) and 90.15 grams of dipotassium phosphate ($\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$) in distilled water and make up to 1 liter.
50. Standard sodium nitrite: Dissolve 1.1 grams of silver nitrite in nitrite-free water. Add a solution of sodium chloride until the silver chloride is completely precipitated. Dilute to 1 liter and allow to settle. Dilute 100 ml. of this solution to one liter and mix well. Finally dilute 50 ml. of the latter solution to 1 liter. Mix and add a few drops of chloroform. 1 ml. = 0.0005 mg. of N = 0.00164 mg. NO_2 .
51. Sulfanilic acid: Dissolve 8.0 grams of pure sulphanilic acid in 750 ml. of water and 250 ml. of glacial acetic acid.
52. Alpha-naphthylamine: Dissolve 5.0 grams of alpha-naphthylamine in a mixture of 750 ml. of water and 250 ml. of glacial acetic acid. Filter through glass wool or cotton.
53. Standard silver sulphate: Dissolve 4.397 grams of C.P. silver sulphate in 1 liter of distilled water. 1 ml. = 1 mg. Cl.
54. Phenoldisulphonic acid. Dissolve 25 grams of pure phenol in 150 ml. of concentrated sulphuric acid and add 75 ml. of fuming sulphuric acid. Heat for 2 hours over a boiling water bath.
55. Sodium hydroxide (approximately 12 N): Dissolve about 480 grams of pure sodium hydroxide in distilled water and make up to about 1 liter.
56. Standard nitrate solution: Dissolve 0.7216 grams of pure potassium nitrate in 1 liter of distilled water. Evaporate 50 ml. of this solution to dryness on the water bath. Moisten the residue with 2 ml. of phenoldisulphonic acid rubbing it well into the residue to insure intimate contact. Dilute to 500 ml. with distilled water. 1 ml. = 0.01 mg. of N = 0.04426 mg. NO_3 .

57. Manganese sulphate: Dissolve 480 grams of manganese sulphate crystals in sufficient distilled water to make 1 liter.
58. Alkaline potassium iodide: Dissolve 500 grams of sodium hydroxide and 150 grams of potassium iodide in sufficient distilled water to make 1 liter.
59. Standard sodium thiosulphate (0.025 N): Dilute the calculated amount of stock standard sodium thiosulphate solution (D) to 1 liter with distilled water. Add 5 ml. of chloroform. Make up fresh every two weeks.

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Normality of stock standard sodium thiosulphate

= ml. of stock standard $\text{Na}_2\text{S}_2\text{O}_3$ required to make 1 liter of 0.025 N sodium thiosulphate.

60. Starch indicator: Make a thin paste of about 2 grams of starch in cold water. Pour into 200 ml. boiling water and stir. When cool add a few drops of chloroform.
61. Potassium permanganate: Dissolve 6.32 grams of potassium permanganate in sufficient water to make 1 liter.
62. Potassium oxalate: Dissolve 20 grams of potassium oxalate in sufficient water to make 1 liter.
63. Sulphuric acid (1 to 3): Add slowly with constant stirring 250 ml. of concentrated sulphuric acid to 750 ml. of distilled water.
64. Standard ammonium oxalate, 0.0125 N: Dissolve exactly 0.8881 grams of pure ammonium oxalate in 1 liter of water.
65. Standard potassium permanganate, 0.0125 N: Dissolve 0.4 grams of potassium permanganate in 1 liter of water and titrate against the ammonium oxalate solution (64) as follows:
 1. Place 100 ml. of distilled water into an Erlenmeyer flask and add 10 ml. of 1 to 3 sulphuric acid (63) and 10 ml. of the potassium permanganate solution.
 2. Place in a boiling water bath for 30 minutes.

3. Add 10 ml. of ammonium oxalate solution (64) and then drop by drop from a burette, add the potassium permanganate solution until the first slight permanent pink color. (No record of the volume of permanganate solution used up to this point need be made.)
4. Heat almost to boiling, add exactly 10 ml. of ammonium oxalate solution (64).
5. Titrate with the permanganate solution to the first pink color, recording the ml. of permanganate solution used.
6. Adjust the permanganate solution so that 1 ml. of oxalate = 1 ml. of permanganate.
66. o-tolidine solution: Place 1 gram of o-tolidine in a large mortar and add 5 ml. of 1 to 4 hydrochloric acid (100 ml. of concentrated hydrochloric acid in 400 ml. of distilled water). Grind to a thin paste and add 150 ml. of distilled water. Stir until the o-tolidine is dissolved. Transfer to a 1 liter graduated cylinder and make up to 505 ml. with distilled water. Add the remaining 495 ml. of 1 to 4 hydrochloric acid.
67. Color standards for chlorine: Solution No. 1: Dissolve 1.5 grams of copper sulphate and 1 ml. of concentrated sulphuric acid in distilled water and make up to 100 ml. Solution No. 2: Dissolve 0.25 grams of potassium dichromate and 1 ml. of concentrated sulphuric acid in distilled water and make up to 1 liter. Place the quantities of the two solutions indicated in the following table in 100 ml. Nessler tubes and make up to the mark with distilled water. Stopper and keep in a dark place.

ml. Soln. No. 1	ml. Soln. No. 2	p.p.m. Cl.
0.4	5.5	0.05
1.8	10.0	0.10
1.9	20.0	0.20
1.9	30.0	0.30
2.0	38.0	0.40
2.0	45.0	0.50
2.0	58.0	0.70

68. Standard sodium thiosulphate (0.001 N): Dilute the calculated amount of stock standard sodium thiosulphate solution (D) to 1 liter with distilled water. Make up fresh every few days.

$$\frac{1}{\text{Normality of stock standard } \text{Na}_2\text{S}_2\text{O}_3} = \text{ml. of}$$

stock standard $\text{Na}_2\text{S}_2\text{O}_3$ required to make 1 liter of 0.001 N sodium thiosulphate.

69. Standard iodine solution, 0.025 N: Dissolve 2.0 grams of potassium iodide crystals in a small quantity of hot, boiled distilled water. Cool, add 3.173 grams of iodine and make up to 1 liter with distilled water. Titrate 25 ml. of this solution with the 0.025 N sodium thiosulphate (59) using starch (60) as an indicator. Adjust the solution so as to be equal to the thiosulphate.

$$\frac{25,000}{\text{ml. thiosulphate used}} = \text{ml. of iodine solution}$$

necessary to produce 1 liter of 0.025 N iodine solution.

70. Cleaning solution: Dissolve 100 grams of commercial potassium dichromate in 375 ml. water and make up to 1 liter with concentrated sulphuric acid. Add the acid to the water solution with constant stirring.

71. Diluting water for biochemical oxygen demand (B.O.D.): Add 6 grams of sodium bicarbonate to 5 gallons of distilled water. Aerate by bubbling air through the water until the dissolved oxygen content is above 7.0 p.p.m. This may require several days. Store for at least two weeks before using.

72. Calibration of bottles: Weigh the bottle empty and again when completely full of distilled water. The difference in weight in grams is the capacity of the bottle in ml.

73. Methylene blue: Dissolve 1 gram of methylene blue (Merck's double zinc salt) in 1 liter of distilled water.

74. Copper sulphate solution (10 per cent). Dissolve 100 grams of copper sulphate crystals in distilled water and make up to 1 liter.
75. Chlorine water: This solution should contain 0.5 grams of chlorine per liter. Make a slightly stronger solution by shaking hypochlorite of lime or sodium hypochlorite with distilled water. Filter and make up to 1 liter. (13 ml. of 3.5 per cent sodium hypochlorite per liter will give approximate strength.) Standardize this solution as follows:
1. Dissolve 2 grams of potassium iodide in 50 ml. of distilled water in an Erlenmeyer flask and add 2 ml. of glacial acetic acid.
 2. Pipette 5 ml. of the chlorine solution into the flask.
 3. Titrate with 0.025 N thiosulphate solution (59) using starch (60) as an indicator near the end of the titration. Calculate the weight of chlorine in 1 liter of solution by multiplying the ml. of thiosulphate by 0.1777.
 4. Dilute the chlorine solution so as to contain 0.5 grams of chlorine per liter, as follows:
$$\frac{500}{\text{Wt. of chlorine per liter}} = \text{ml. of chlorine}$$
solution to give 1 liter of solution containing 0.5 grams Cl.
76. Hydrochloric acid (approximately 1 N): Dilute 86 ml. of concentrated hydrochloric acid with sufficient distilled water to make 1 liter of solution.
77. Molybdate solution: Dissolve 100 grams of molybdic acid in dilute ammonium hydroxide (144 ml. of concentrated ammonium hydroxide and 271 ml. of water). Pour this solution slowly with constant stirring into dilute nitric acid (489 ml. of concentrated nitric acid and 1148 ml. of distilled water). Keep the mixture in a warm place for several days or until a portion heated to 40

phosphomolybdate. Decant the solution from any sediment and preserve in a glass-stoppered bottle. Before using, add 5 ml. of concentrated nitric acid to 100 ml. of the molybdate solution and filter.

78. Standard sodium hydroxide (0.3238 N): Dilute the calculated amount of stock standard sodium hydroxide (B) to 1 liter with boiled distilled water.

$$\frac{323.8}{\text{Normality of stock standard NaOH}} = \text{ml. of stock}$$

standard NaOH necessary to make 1 liter of 0.3238 N NaOH.

79. Standard hydrochloric acid (0.3238 N): Dilute the calculated amount of stock standard hydrochloric acid (C) to 1 liter with distilled water.

$$\frac{323.8}{\text{Normality of standard stock HCl}} = \text{ml. stock}$$

standard HCl necessary to make 1 liter of 0.3238 N HCl.

80. Salicylic acid mixture: Dissolve 1 gram salicylic acid in 30 ml. of concentrated sulphuric acid.

81. Boric acid: Dissolve 40 grams of boric acid in 1 liter of distilled water.

82. Standard hydrochloric acid (0.5 N): Dilute the calculated amount of stock standard hydrochloric acid (C) to 1 liter with distilled water.

$$\frac{500}{\text{Normality of standard stock HCl}} = \text{ml. of stock}$$

standard HCl necessary to make 1 liter of 0.5 N HCl.

83. Potassium hydroxide for CO₂: Dissolve 100 grams of pure potassium hydroxide in 200 ml. of distilled water.

84. Phenolphthalein for cyanides: (Not phenolphthalein): Dissolve 0.5 grams of phenolphthalein (Eastman Kodak Co.) in about 150 ml. of dilute sodium hydroxide (about 1 gm. NaOH in 150 ml. of distilled water). Keep in a dark place.

85. Copper sulphate (0.05 per cent): Dissolve 0.5 grams of copper sulphate crystals in 1 liter of distilled water.
86. Sodium hydroxide (0.2 N): Dilute the calculated amount of stock standard sodium hydroxide (B) to 1 liter with boiled distilled water.

200 = ml. stock
Normality of standard stock NaOH

standard NaOH necessary to make 1 liter of 0.1 N NaOH.

87. Thymolphthalein: Prepare a stock solution by grinding 0.4 grams of thymolphthalein with 17.2 ml. of 0.05 N sodium hydroxide (12) and make up to 100 ml. with distilled water. For use, dilute 10 ml. of this stock solution to 100 ml. with distilled water.
88. Buffer solution for phenols: Dissolve about 6.2 grams of boric acid and 7.45 grams of potassium chloride in 1500 ml. of distilled water. Adjust with 0.2 N sodium hydroxide (86) to such a strength that 5 ml. when added to 100 ml. of the distilled will give a pH of 9.6. This buffer is to be used with samples of low phenol content.
89. Standard phenol solution: First prepare a standard stock phenol solution by dissolving 1 gram of pure phenol in 1 liter of distilled water. Standardize as follows:
 1. Pipette 50 ml. of the well mixed phenol solution into an Erlenmeyer flask.
 2. Add 50 ml. of 0.1 N bromine (93) and 5 ml. of concentrated hydrochloric acid.
 3. Allow to stand in cool water for 15 minutes and add 2 grams of potassium iodide crystals.
 4. Titrate with 0.1 N sodium thiosulphate (92) using starch (60) as an indicator near the end of the titration.
Record the ml. of thiosulphate used.
 $(50 - \text{ml. } 0.1 \text{ N thiosulphate}) \times 0.156 = \text{mg. phenol per ml.}$

To make a standard solution in which 1 ml. = 0.01 mg. of phenol, dilute the standard stock solution with distilled water as follows:

$$\frac{10}{\text{mg. phenol per ml.}} = \text{ml. of standard stock phenol}$$

solution necessary to make 1 liter of standard phenol solution.

$$1 \text{ ml.} = 0.01 \text{ mg. phenol.}$$

90. 2,6-dibromoquinonechloroimide: Dissolve 0.1 grams of the powder in 25 ml. of 95% ethyl alcohol and place in a tightly stoppered brown bottle. This stock solution must be made up fresh every 3 days. Before the test is made, dilute 10 ml. of the stock solution to 200 ml. with distilled water. This solution will not last over 30 minutes.
91. Sodium hydroxide (20 per cent): Dissolve 100 grams of sodium hydroxide in 400 ml. of distilled water.
92. Sodium thiosulphate (0.1 N): Dilute to 1 liter with distilled water, the calculated amount of stock standard sodium thiosulphate solution (D).

$$\frac{100}{\text{Normality of stock standard thiosulphate}} = \text{ml.}$$

stock standard sodium thiosulphate necessary to make 1 liter of 0.1 N sodium thiosulphate.

93. Bromine (0.1 N): Dissolve exactly 2.784 grams of potassium bromate and 10 grams of potassium bromide in distilled water and make up to 1 liter. Standardize as follows:

1. Pipette 25 ml. of the well mixed bromine solution into an Erlenmeyer flask.
2. Add about 75 ml. of distilled water and 5 ml. of concentrated hydrochloric acid.
3. Add 2 grams of potassium iodide crystals and titrate against the 0.1 N sodium thiosulphate solution (92) using starch (60) near the end of the titration.

4. Adjust the solution by diluting with distilled water in the proportion indicated below so that 1 ml. bromine solution = 1 ml. thiosulphate solution.

$$\frac{25,000}{\text{ml. of thiosulphate used}} = \text{ml. bromine solu-}$$

tion necessary to make 1 liter of 0.1 N bromine.

94. Potassium permanganate (0.1 N): Dilute the calculated amount of stock standard potassium permanganate solution (E) to 1 liter with distilled water.

$$\frac{100}{\text{Normality of stock standard KMnO}_4} = \text{ml. stock}$$

standard KMnO_4 necessary to make 1 liter of 0.1 N potassium permanganate.

95. Sulphuric acid (0.1 N): Dilute the calculated amount of the stock standard sulphuric acid solution (A) to 1 liter with distilled water.

$$\frac{100}{\text{Normality of stock standard H}_2\text{SO}_4} = \text{ml. of stock}$$

standard H_2SO_4 necessary to make 1 liter of 0.1 N sulphuric acid.

96. Approximately 0.2 N hydrochloric: Dilute 17 ml. of concentrated hydrochloric acid to 1 liter with distilled water.

97. Approximately 0.2 N sodium hydroxide: Dissolve 8 grams of sodium hydroxide in 1 liter of distilled water.

98. Phosphoric acid, 10 per cent: Dilute 118 ml. of 85 per cent phosphoric acid to 1 liter with distilled water.

99. Phosphoric acid, 50 per cent: Dilute 118 ml. of 85 per cent phosphoric acid to 200 ml. with distilled water.

100. Copper sulphate solution: Dissolve about 0.05 grams of copper sulphate in 1 liter of distilled water.

101. Strong buffer solution for phenol: Dissolve about 6.2 grams of boric acid and 7.45 grams of potassium chloride in 1500 ml. of distilled water. Adjust with 0.2 N sodium hydroxide (86) to such a strength that 1 ml. when added to 100 ml. of distilled water will give a pH of 9.6. This buffer solution is to be used with samples having high phenol contents.
102. Ferric chloride 10%. If anhydrous ferric chloride is used, dissolve 40 grams of the salt in 1 liter of distilled water. If crystalline ferric chloride is used, dissolve 67 grams of the crystals in 1 liter of water.



SECTION III

CHEMISTRY AND DISCUSSION OF METHODS

Foreword

The work in the preceding sections of this book has been confined to instructions for carrying out certain chemical analytical determinations on water, sewage and trade wastes. The instructions were made sufficiently detailed and clear so that they could be followed without referring to other explanations. It is necessary in many instances for the laboratory worker to understand a certain amount of chemistry in order that he may intelligently apply even detailed instructions. A certain facility in carrying through instructions for the procedure for analytical determinations may be acquired by practice but the analyst should not be content until he understands the reasons upon which the procedures have been formulated. Many laboratory workers will no doubt find that they are thoroughly familiar with the material contained in this section as it is intended only as a very elementary treatise of the chemistry which is considered essential in order to acquire a fair understanding of the analytical determinations given in this book.

This section will cover explanations of units used in chemistry, the writing of formulae and equations, methods of expressing results, reactions involved in the determinations and other fundamental relations.

Fundamentals

Units of measurement

The ordinary units of measurement used in laboratory work are based on the metric system. It is sometimes necessary to convert values from the metric system to the English system or vice versa. Convenient conversion values are given later in this discussion.

The unit of weight is the kilogram. There are 1000 grams in one kilogram and 1000 milligrams in one gram. Thus, there are 1,000,000 milligrams in one kilogram.

The unit of volume is the liter. It is the volume of 1 kilogram of pure water at a temperature of 4°C and 76 cm. of mercury pressure. There are 1000 milliliters in 1 liter. Therefore, 1 milliliter of water weighs one gram. This relation of weight and volume makes the use of metric units very convenient in the laboratory. This relation is not quite true for other temperatures and pressures but the effect of these factors may be neglected in ordinary work. The term cubic centimeter (cc.) is often used in place of milliliter (ml.). For all practical purposes they may be considered identical. (The milliliter is slightly larger.)

The unit of length is the meter. There are 100 centimeters (cm.) in the meter and 10 millimeter (mm.) in the centimeter. There are thus 1000 millimeters in 1 meter.

Temperatures are generally recorded in degrees Centigrade. Zero degrees of the Centigrade thermometer is the freezing point of water and 100 degrees is the boiling point of water. These values correspond to 32 degrees and 212 degrees respectively on the Fahrenheit scale.

The results of the chemical analysis of water and sewage are usually expressed in parts per million (p.p.m.) by weight. One liter of water or sewage to be analyzed, with its contained impurities, is

assumed to weigh one kilogram as it is used in the laboratory. It will be noticed from the weight relations given above that one p.p.m. is the same as one milligram per liter. This is a convenient relation to have in mind when performing certain calculations. In special cases of waters containing large amounts of impurities, the results obtained should be divided by the specific gravity of the sample.

The results may also be expressed in grains per gallon. One grain per gallon (g.p.g.) is equivalent to 17.12 p.p.m. The following conversion factors will be found convenient.

$$1 \text{ milligram per liter} = 1 \text{ part per million} \\ (\text{p.p.m.})$$

$$1 \text{ grain per gallon (g.p.g.)} = 17.12 \text{ p.p.m.}$$

$$1 \text{ part per million} = 8.345 \text{ lbs. per million gallons}$$

$$1 \text{ liter} = 0.2642 \text{ gallons}$$

$$1 \text{ kilogram} = 2.205 \text{ pounds}$$

$$1 \text{ pound} = 453.6 \text{ grams}$$

$$1 \text{ meter} = 39.37 \text{ inches}$$

$$1 \text{ degree Centigrade} = 1.8 \text{ degrees Fahrenheit}$$

Other conversion factors will be found on page 193 of the Appendix.

Chemistry

All matter is made up of one or more elements. The elements are fundamental substances which cannot be divided into simpler substances. Compounds are substances consisting of elements chemically combined. The elements are designated by abbreviations or symbols such as O for oxygen, H for hydrogen, S for sulphur, etc.

The atoms of an element have a definite weight called the atomic weight. The atomic weights are based on oxygen as 16 in which case the atomic weight of hydrogen is 1.008. A list of the elements encountered in water and sewage analyses and their atomic weights is given in the Appendix page 189.

Elements combine in definite proportions to

form compounds. The make-up of a compound is indicated by its formula which is a combination of the symbols of the elements. Thus, water is composed of two atoms of hydrogen and one atom of oxygen and its formula is H_2O . Sulphuric acid is composed of two atoms of hydrogen, one of sulphur and four of oxygen and its formula is H_2SO_4 . The symbol for an element indicates also one atom and likewise the formula for a compound indicates one molecule. Thus $2H$ indicates two atoms of hydrogen and $2H_2SO_4$ indicates two molecules of sulphuric acid. The molecular weight of a compound is equal to the sum of the atomic weights of the atoms in the molecule. Thus a molecule of water (H_2O) has a molecular weight of $(2 \times 1.008) + 16.00 = 18.016$.

The combining power or ratio in which atoms of an element combine with atoms of other elements is called valence. The valence of hydrogen is one. The valence of the other elements is determined by an examination of the formula of a compound in which the element occurs. Oxygen, for instance, has a valence of two since it occurs in water combined with two hydrogen atoms (H_2O). Chlorine has a valence of one since it occurs in HCl combined with one hydrogen atom.

Not all elements will combine to form compounds. For instance, hydrogen will combine with oxygen, chlorine and nitrogen, but will not combine with metals such as iron, calcium and sodium. The bond or force which holds elements together in compounds is electrical in nature and elements having like electrical tendencies will not combine. Thus, hydrogen and the metals are said to have positive electrical tendencies and chlorine, oxygen, etc., negative. The comparative value of these electrical forces constitute the valence of the atoms. Hydrogen is said to have a positive valence of one, oxygen a negative valence of two, etc. The sum of the positive and negative valences in any compound must be equal. Thus, in H_2SO_4 , the oxygen has a total negative valence of

eight and hydrogen positive two, leaving six positive for the sulphur. A few elements assume different valences under different conditions. Carbon may have positive valence of two or four in carbon monoxide (CO) and carbon dioxide (CO_2) respectively. One element encountered in water and sewage analysis may have either a positive or negative valence. For instance, N has a negative valence of three in NH_3 and a positive valence of four in NO_2 .

The atomic and molecular weights are the basis of all quantitative chemical reactions and are used in all quantitative calculations. A knowledge of them is necessary in order to understand the calculations involved in the chemical determinations. For example, the formula for sulphuric acid is H_2SO_4 . The molecular weight of H_2SO_4 and percentage composition of the elements in this compound may be obtained by referring to the atomic weights as follows:

$$\text{Hydrogen } 2 \text{ atomic weights} = 2 \times 1.008 = 2.016$$

$$\text{Sulphur } 1 \text{ atomic weight} = 1 \times 32.06 = 32.060$$

$$\text{Oxygen } 4 \text{ atomic weights} = 4 \times 16.00 = \underline{\underline{64.000}}$$

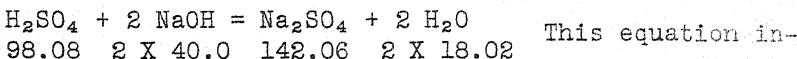
$$\text{Molecular weight} = 98.076$$

$$\text{The per cent by weight of hydrogen is } \frac{2.016}{98.076} \times 100$$

$$= 2.04 \text{ and of sulphur is } \frac{32.06}{98.076} \times 100 = 32.69 \text{ and of}$$

$$\text{oxygen is } \frac{64.00}{98.076} \times 100 = 65.36.$$

The chemical reaction and the relative weights of the reacting substances is shown by writing an equation using the formulae and molecular weights as follows:



dicates that one molecule of sulphuric acid reacts with two molecules of sodium hydroxide to form one molecule of sodium sulphate and two molecules of wa-

written below the formulae indicate the weight ratios between the reacting substances. Thus 98.08 grams (pounds, tons or other weight units) of sulphuric acid reacts with 80.0 grams of sodium hydroxide to form 142.06 grams of sodium sulphate and 36.04 grams of water. These weight ratios may be used to solve problems similar to the one which follows.

Example

How much sodium hydroxide will react with 100 lbs. of sulphuric acid?

Solution

Let A = the lbs. of sodium hydroxide

$$\text{Then } \frac{A}{100} = \frac{80.00}{98.08}$$

$$A = 100 \times \frac{80.00}{98.08} = 81.6 \text{ lbs. of sodium hydroxide.}$$

In all cases, knowing the equation for a given reaction, the weight ratios can be determined from the atomic weights of the elements and the formula of the compounds involved. Knowing the weight ratios, if the actual weight of any one compound entering into the reaction is known, the weights of all of the other compounds involved can be determined. A list of chemical formulae and equations encountered in water and sewage analysis is given in the Appendix pages 190 and 192.

The Normal System

Some of the more important determinations in water and sewage analysis are dependent upon the use of standard solutions. A standard solution is one which contains a known weight of the active substance dissolved in a definite volume of solution. Methods involving the use of such solutions are known as volumetric procedures since the quantitative result is obtained by measurement of volumes.

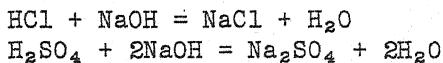
In the water and sewage laboratory, it is convenient to have solutions of certain definite

strengths for use in the different determinations. Such solutions simplify the calculation of results which is a decided advantage in routine analysis. They can best be prepared by diluting portions of stock solutions in such a manner as to give solutions of the desired strength.

The strength of a standard solution is usually expressed in terms of the normal system. A normal solution is one which contains one gram-equivalent weight of the active substance in one liter of solution. The gram-equivalent weight of a substance is the weight of that substance which is equivalent to one gram of hydrogen.

There are two general types of chemical reactions encountered in the volumetric determinations used for water and sewage analysis, (1) the simple neutralization or double-decomposition reactions, (2) the reactions involving oxidation and reduction.

The former reactions involve a change in the position of the various atoms and groups making up the reacting substances. The following equations illustrate this type of reaction.



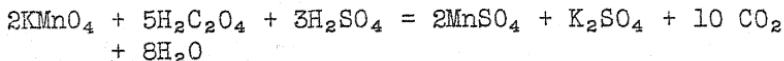
In a reaction of this type, the gram-equivalent weight of the compounds reacting is calculated by dividing the molecular weight of the compound by the number of replaceable hydrogen atoms or their equivalent in that compound.

Molecular weight of a substance
No. of replaceable hydrogen atoms or their equivalent
= gram-equivalent weight of the substance.

Thus the gram-equivalent weight of HCl is 35.5, since the molecular weight (35.5) is divided by one, because there is one replaceable hydrogen. The gram-equivalent weight of H_2SO_4 is one half its molecular weight, or 49, because there are two replaceable

hydrogens. In NaOH one Na can be replaced by one H and is equivalent to one atom of hydrogen. Therefore, the gram-equivalent weight of NaOH is 40 (molecular weight divided by one).

The second type of reaction, oxidation-reduction, is illustrated by the following equation:



A study of the equation will show that there is more involved than a simple rearrangement of atoms and groups. Mn, for instance, has a positive valence of seven in KMnO_4 , but only two in MnSO_4 . The Mn has lost five positive valences (has been reduced) and the KMnO_4 has a change in valence of five. Likewise, each C atom in $\text{H}_2\text{C}_2\text{O}_4$ has a valence of positive three and in CO_2 a valence of positive four. The compound $\text{H}_2\text{C}_2\text{O}_4$ has, therefore, a change in positive valence of two (one for each of the two C atoms).

The gram-equivalent weight of a compound entering into an oxidation-reduction reaction is equal to its molecular weight divided by the change in valence of that compound.

$$\frac{\text{molecular weight}}{\text{change in valence}} = \text{gram-equivalent weight.}$$

The gram-equivalent weight of KMnO_4 is 31.6 (158 divided by 5) and of $\text{H}_2\text{C}_2\text{O}_4$ is 45 (90 divided by 2).

A number of reactions of these two types and the gram-equivalent weights of the compounds involved are given in the Appendix pages 190 and 192.

The normality of a standard solution is the ratio of the weight in grams of the substance in one liter to the gram-equivalent weight.

$$\frac{\text{weight in grams per liter}}{\text{gram-equivalent weight}} = \text{normality (N)}$$

Solutions of equal normalities are equal in their reacting value, volume per volume. That is, a

volume of 0.1 N hydrochloric acid will react with the same volume of 0.1 N sodium hydroxide.

The use of normalities simplifies the calculations necessary in obtaining the results of a volumetric analysis. For example, a sample of a solution of iodine is titrated with 0.1 N sodium thiosulphate. Ten ml. of the thiosulphate are required to react with the iodine. It can then be assumed that the amount of iodine present was that which would be contained in 10 ml. of a 0.1 N iodine solution. The equivalent weight of iodine is 127.9. One liter of 0.1 N iodine would contain 12.79 grams of iodine or 10 ml. would contain 0.1279 grams. Thus, the sample used contained 0.1279 grams of iodine.

Standard Solutions

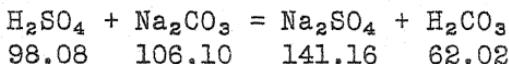
Stock solutions should always be made stronger than those to be used in the various determinations. Strong solutions usually keep better than weak ones. In preparing the standard solutions for use in the various tests, the stronger solution may be diluted to give the desired normality. The portion of a stock solution required to make one liter of a desired normality may be calculated as follows:

$$\frac{1000 \times \text{desired normality}}{\text{normality of stock solution}} = \text{ml. of stock solution.}$$

Standard stock solutions of some chemicals may be made by direct weight since the chemical can be obtained in a pure state. An example is anhydrous sodium carbonate. Others such as sulphuric acid and potassium permanganate must be standardized by titration against some pure chemical.

Stock standard acid solutions can be prepared by titrating against anhydrous sodium carbonate. The best grade of C.P. anhydrous sodium carbonate must be used. Methyl orange is used as an indicator.

The reaction involved in this titration is represented by the following equation:



The method for calculating the normality of the acid solution from the results of the titration can best be illustrated by a typical problem.

Example

Weight of sodium carbonate used, 0.2138 grams.

Volume of sulphuric acid solution required for the titration, 37.1 ml.

Solution

$$\text{Equivalent weight of H}_2\text{SO}_4 = \frac{98.08}{2} = 49.04$$

$$\text{Equivalent weight of Na}_2\text{CO}_3 = \frac{106.10}{2} = 53.05$$

(1) 0.2138 grams of Na_2CO_3 is equivalent to $\frac{49.04}{53.05}$

$$X 0.2138 = 0.1976 \text{ grams H}_2\text{SO}_4.$$

(2) 0.1976 grams H_2SO_4 was in 37.1 ml. of solution
 $\frac{0.1976}{37.1} X 1000 = 5.326$ grams H_2SO_4 in 1 liter of solution.

(3) $\frac{5.326}{49.04} = 0.1086$ the normality of the acid solution.

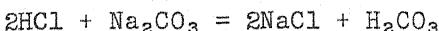
If the three steps above were placed in one equation it would read as follows:

$$\frac{49.04 X 0.2138 X 1000}{53.05 X 37.1 X 49.04} = 0.1086 \text{ N}$$

The general formula would, therefore, be:

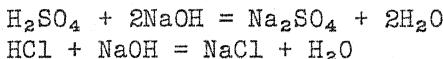
$$\frac{\text{weight of Na}_2\text{CO}_3 X 1000}{\text{ml. of H}_2\text{SO}_4 X 53.05} = \text{normality of acid solution.}$$

The same method is used in the standardization of hydrochloric acid.



The same general formula given above may be used in calculating the results.

The stock standard solution of sodium hydroxide is usually prepared by titrating against a standard acid solution.



The normality of the solution is calculated as illustrated in the following example using the sulphuric acid, the strength of which was calculated above.

Example

Volume of NaOH used = 25 ml.

Volume of H₂SO₄ used = 33.4 ml.

Normality of H₂SO₄ used = 0.1086

Solution

(1) 0.1086 N H₂SO₄ contains 0.1086 X 49.04 = 5.326

grams H₂SO₄ per liter or $\frac{5.326}{1000} = 0.005326$ grams

per ml.

(2) 33.4 X 0.005326 = 0.1779 grams H₂SO₄ used in the titration.

(3) The equivalent weight of NaOH is 40.05
The equivalent weight of H₂SO₄ is 49.04

0.1779 grams H₂SO₄ is equivalent to $\frac{40.05}{49.04} \times 0.1779 = 0.1450$ grams NaOH.

(4) 0.1450 grams NaOH in 25 ml. = 5.800 grams NaOH per liter.

(5) $\frac{5.800}{40.05} = 0.1450$ N the normality of the NaOH.

Combining the above 5 steps:

$$\frac{0.1086 \times 49.04 \times 33.4 \times 40.05 \times 1000}{1000 \times 49.04 \times 25 \times 40.05} = 0.1450 \text{ N}$$

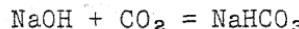
The general formula derived above is:

$$\frac{\text{normality of acid} \times \text{ml. of acid}}{\text{ml. of NaOH}} = \frac{\text{normality of}}{\text{NaOH}}$$

This is a general formula which is applicable to all titrations involving two solutions when using the normal system. The formula may be restated as follows:

ml. of one solution X its normality = ml. of the other solution X its normality.

Sodium hydroxide solution must be made up with carbon dioxide-free water because of the reaction of the NaOH with the CO₂.

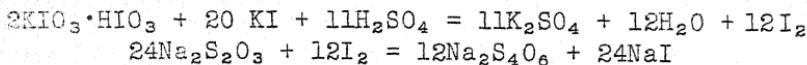


The solution also deteriorates if not kept free from carbon dioxide.

Stock standard sodium thiosulphate may be prepared of sufficient accuracy for some determinations, such as dissolved oxygen, by direct weight of the unweathered crystals. The equivalent weight of crystallized sodium thiosulphate, Na₂S₂O₃·5H₂O, is 248.12. Therefore, 248.12 grams of the crystals are required for 1 liter of 1 N sodium thiosulphate.

For a more accurate standardization or for re-standardization of a previously prepared solution, titration against a weighed amount of potassium biniodate (KIO₃·HIO₃) may be conveniently used.

The reactions involved are as follows:



These two equations show that one molecule of potassium biniodate is equivalent to 12 molecules of sodium thiosulphate. The equivalent weight of biniodate is its molecular weight divided by 12 or $\frac{390}{12} = 32.50$.

The general formula for calculating the normality of the thiosulphate from the weight of biniodate and the titration results may be derived in the same manner as used for the acid solution previously described. This general formula is:

$$\frac{\text{weight of biniodate used (grams)} \times 1000}{\text{ml. of thiosulphate}} = \text{normality}$$

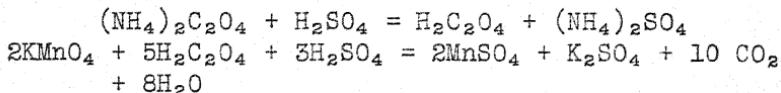
$$\text{ml. of thiosulphate} \times 32.5$$

of sodium thiosulphate.

A standard solution of ammonium oxalate may be prepared by a direct weight of the pure crystals $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The equivalent weight is the molecular weight divided by two or $\frac{142.1}{2} = 71.05$. Solu-

tions of ammonium oxalate are not stable and should be prepared fresh about every two weeks.

Standard solutions of potassium permanganate are prepared by titration against ammonium oxalate solutions. The equations for the reactions are:



This reaction has been discussed previously as an oxidation-reduction reaction.

The derivation of the formula for calculating the normality of the permanganate solution from the results of the titration is the same as that used for the standardization of sodium hydroxide previously discussed except that the equivalent weights of potassium permanganate (31.60) and ammonium oxalate (62.04) are used. The general formula is:

$$\frac{\text{normality of oxalate} \times \text{ml. of oxalate}}{\text{ml. of permanganate}} = \text{normality of permanganate}$$

Alkalinity and Acidity

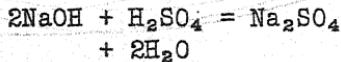
Alkalinity

There are three kinds of alkalinity, hydroxide (OH), normal carbonate (CO_3), bicarbonate (HCO_3). Normal carbonate is also called mono-carbonate. In order to distinguish between the kinds of alkalinity present in a sample and to determine the quantities of each, a titration is made with a standard acid using two indicators successively. The indicators used are phenolphthalein and methyl orange. Phenolphthalein gives a pink color only in the presence of hydroxide or normal carbonate. Methyl orange is yellow in the presence of any of the three types of alkalinity.

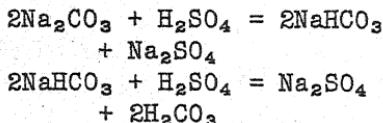
Normal carbonate alkalinity may be present with either hydroxide or bicarbonate alkalinity, but hydroxide and bicarbonate cannot be present together in the same sample. If there is phenolphthalein alkalinity in a sample it is due to the presence of either hydroxide or normal carbonate or both. If there is methyl orange alkalinity present it is due to any one of the three碱alinitiess, or hydroxide and normal carbonate together, or normal carbonate and bicarbonate together.

The following equations illustrate the reactions occurring when each of the three types of alkalinity are titrated with an acid.

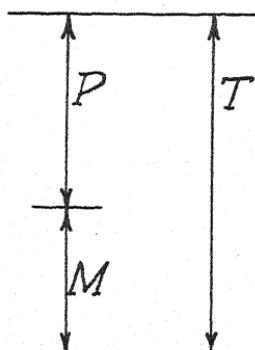
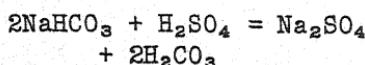
(1) Hydroxide



(2) Normal carbonate



(3) Bicarbonate



P represents the alkalinity as shown by phenolphthalein.

T represents the total alkalinity or that shown by methyl orange.

M = T - P or the additional alkalinity shown by methyl orange beyond that shown by phenolphthalein.

There are five alkalinity conditions possible in a sample: (1) hydroxide alone, (2) hydroxide and normal carbonate, (3) normal carbonate alone, (4) normal carbonate and bicarbonate, (5) bicarbonate alone. These five conditions may be distinguished and the quantities determined from the results of acid titrations by the following method:

Condition (1) is fulfilled when $P = T$ ($M = \text{zero}$), because P indicates either hydroxide or normal carbonate, but normal carbonate would give a positive value for M since the phenolphthalein end-point occurs when one half of the normal carbonate reaction is completed. If $M = \text{zero}$ there can be no normal carbonate present.

Condition (2) is fulfilled when P is greater than $1/2 T$, but less than T, or M is greater than zero. Since M is greater than zero there must be some normal carbonate alkalinity present. M measures one half of the normal carbonate, therefore, the normal carbonate equals $2M = 2(T - P)$. But the condition states that P is greater than $1/2 T$ or greater than $2M$, therefore, there must be some hydroxide alkalinity present. The hydroxide alkalinity equals the total alkalinity minus the normal carbonate alkalinity or $T - 2(T - P) = 2P - T$.

Condition (3) is fulfilled when $P = 1/2 T$ or ($P = M$). Since M represents one half of the normal carbonate and $P = M$ then P must represent the other half and only normal carbonate can be present. Normal carbonate = $2P = T$.

Condition (4) is fulfilled when P is less than $1/2 T$ (M is greater than P). M can be greater than P only when bicarbonate is present in addition to normal carbonate. This precludes hydroxide. The

alkalinity represented by P is due to one half of the normal carbonate. Then $2P =$ normal carbonate and the bicarbonate = $T - 2P$.

Condition (5) is fulfilled when P = zero. In this case there can be no hydroxide or normal carbonate. The alkalinity is all bicarbonate = T.

In the alkalinity determination the sample is titrated with 0.02 N sulphuric acid. P in the above discussion represents the ml. of acid used for the phenolphthalein titration and M the additional ml. of acid used for the methyl orange titration. T represents the total ml. of acid used for the alkalinity ($P + M$).

If the results of the titration of a 100 ml. sample are substituted in the correct condition above and these results multiplied by 10, the values obtained will be in p.p.m. of the specific alkalinity in terms of CaCO_3 . (Alkalinites are usually expressed in terms of CaCO_3 .) The factor 10 is used because one ml. of 0.02 N sulphuric acid is equal to one mg. of CaCO_3 . If a 100 ml. sample is used one ml. of acid would represent one mg. of CaCO_3 per 100 ml. or 10 mg. per liter or 10 p.p.m.

Problem

Why is one ml. of 0.02 N sulphuric acid equal to one mg. CaCO_3 ?

Solution

The equivalent weight of H_2SO_4 = 49.04

The equivalent weight of CaCO_3 = 50.05

(1) One liter of 0.02 N H_2SO_4 contains 49.04 X 0.02 = 0.9808 grams of H_2SO_4 or one ml. contains 0.0009808 gms. or 0.9808 mg. H_2SO_4 .

(2) One ml. of 0.02 N H_2SO_4 is then equivalent to

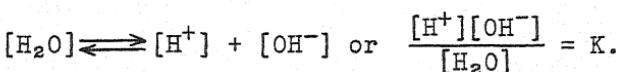
$$\frac{50.05}{49.04} \times 0.9808 = 1.00 \text{ mg. of } \text{CaCO}_3$$

Hydrogen-ion concentration (pH)

The pH determination is used in the control of

water and sewage treatment processes. In order to properly interpret the results of a pH determination it is essential to have a knowledge of the meaning of the term and an idea of the value of the readings in terms of acidity and alkalinity. pH is defined as the "logarithm (base 10) of the reciprocal of the hydrogen-ion concentration." The "concentration" of the hydrogen ion is expressed in molecular weights (mols) per liter. Since the molecular weight of the hydrogen ion is 1, a solution containing 1 gram of hydrogen-ion per liter would have a concentration of 1. The term "concentration of hydrogen-ion" is written thus $[H^+]$. The brackets mean "concentration" and the H^+ means "Hydrogen-ion."

Water (H_2O) breaks down (dissociates) to a very slight extent into electrically charged particles called "ions", thus $HOH = H^+ + OH^-$. The H ion carries a positive charge and the OH a negative. There is an equilibrium established for any given condition when the rate of dissociation of the H_2O molecule into H^+ and OH^- is equal to the rate of association of H^+ and OH^- into the molecule H_2O . This may be written thus,



This last equation means that at equilibrium the product of the concentration of H^+ ion X OH^- ion divided by the concentration of the undissociated H_2O molecule is equal to a constant (K). The value of $[H_2O]$ is so large in comparison to the dissociated ions that it can be given a constant value (w). The equation then reads $[H^+][OH^-] = Kw$.

Kw has been proven by experiment to be

$$\frac{1}{100,000,000,000,000} \text{ or } \frac{1}{10^{14}}. \text{ One over a number with}$$

a positive exponent is equal to the number with the same negative exponent, hence $Kw = 10^{-14}$. In pure water, then, $[H^+] = 10^{-7}$ and $[OH^-] = 10^{-7}$. The

logarithmn of $10^{-7} = -7$ but in its use to indicate pH the negative sign is omitted, therefore, in pure water $[H^+] = \text{pH } 7$. Such a solution is neutral and has no excess of either H^+ or OH^- .

In any solution in order to maintain the equilibrium $[H^+][OH^-] = 10^{-14}$, if the $[H^+]$ is increased the $[OH^-]$ must be decreased accordingly. For example if $[H^+]$ is increased to 10^{-4} then $[OH^-]$ must be decreased to 10^{-10} ($10^{-4} \times 10^{-10} = 10^{-14}$). The pH in this case would be 4. An excess of H^+ is indicated by a pH below 7 and the solution is said to be acid. pH values above 7 indicate an excess of OH^- or an alkaline condition.

As the pH values extend further from pH 7 the acidity or alkalinity increases. The increase is not in direct proportion to the pH values but are logarithmic functions of those values. That is, a solution with a pH of 5 is 10 times as acid as one with pH 6, and one with pH 4 is 100 times as acid as one with a pH of 6.

pH and titratable acidity are not the same except in cases where the acid or acid salts in the solution are completely ionized. In water and sewage the compounds are present in such minute amounts that the pH and titratable acid are more nearly the same than in stronger solutions. There are many factors, however, affecting the ionization of compounds and hence the pH, but these can not be discussed here.

For completely ionized solutions, the following comparison can be made between the normalities of acid solutions and pH. These values are based on the fact that in a completely ionized normal acid solution there is one gram of hydrogen ion per liter.

pH	Normality of completely ionized acid
3.0	0.001
4.0	0.0001
5.0	0.00001
6.0	0.000001

Two general methods are available for the determination of pH, namely, the electrometric and colorimetric. There are two types of electrometric apparatus, one using a hydrogen electrode, the other a quinhydrone electrode. Electrometric methods are convenient for use for solutions where color changes are difficult or impossible to determine.

Colorimetric methods make use of the changes in color which certain dyes undergo under various changes in hydrogen-ion concentration. This change in color is not complete with a very small change in pH, but extends over a comparatively wide range of pH. Indicators have certain definite pH ranges for color change and the indicator selected should be governed by the pH of the sample tested. The accuracy of the indicator is greatest near the center of its range and decreases as the limits are approached. The following are some indicators and the pH ranges covered by them.

Indicator	pH range
Chlorphenol red	5.2 to 6.8
Bromthymol blue	6.0 to 7.6
Phenol red	6.8 to 8.4
Cresol red	7.2 to 8.8
Thymol blue	8.0 to 9.6

Coagulants and Coagulation

Coagulants are used in nearly all water treatment plants and in some sewage treatment plants. They are used (1) to remove natural suspended and colloidal material, (2) to remove chemicals which do not settle readily in chemical treatment processes, (3) to assist in filtration by forming mats on sand filters and (4) to assist in the vacuum filtration of sewage sludge.

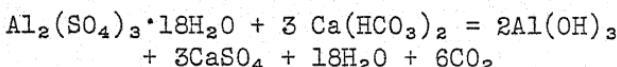
A coagulant reacts with the natural alkalinity in solution in the liquid treated, or with other added chemicals, to form an insoluble flocculant

precipitate. The precipitate clarifies the liquid by coagulating, absorbing and entraining suspended and colloidal material and also may remove colors and gases in solution. A portion of the precipitate formed in water filtration plants is carried through the sedimentation basins to be deposited on the filter beds where it further assists in the clarification of the water and removal of color, odor and taste producing compounds.

The chemicals most commonly used as coagulants in water treatment are aluminum sulphate (alum), iron sulphate (copperas), iron chloride and sodium aluminate. Their use results in the formation of the hydroxides or aluminates which are the effective coagulating agents. In some waters containing magnesium use is made of the magnesium hydroxide formed as the effective coagulating agent.

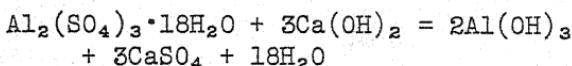
Alum is the coagulant most widely used. Alum reacts with the natural alkalinity of the water or, if the alkalinity is insufficient, with the added alkalinity in the form of lime, $\text{Ca}(\text{OH})_2$, or soda ash, Na_2CO_3 , producing a precipitate which is usually considered to be aluminum hydroxide. Ordinarily there is sufficient natural alkalinity present to react with the coagulant. The reactions follow:

(1) Alum and natural alkalinity.

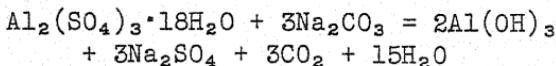


(2) Alum and added alkalinity.

(a) Alum and lime



(b) Alum and soda ash

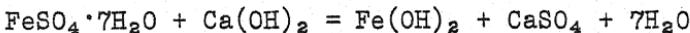


The amount of alum or other chemicals cannot be exactly determined from the above equations as there are too many variables effecting the reactions. Actual

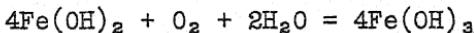
plant experience is necessary with each particular water. Generally the amount of alum used is from 0.3 to 3 grains per gallon although some waters require less than 0.2 and others as high as 10 grains per gallon. The theoretical amounts of alkalinites, as required by the above equations, for each grain per gallon of alum used are:

(1) Natural alkalinity (as CaCO_3)	0.4505	grains per gallon
(2) (a) Lime as CaO	0.2524	" " "
Lime as Ca(OH)_2	0.3336	" " "
(b) Soda ash as Na_2CO_3	0.4773	" " "

Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, requires the addition of lime. The reaction follows:



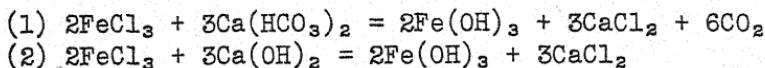
The dissolved oxygen present in the water oxidizes the ferrous hydroxide, to ferric hydroxide as follows:



The ferric hydroxide is an insoluble effective coagulant. The use of this iron and lime treatment process requires careful regulation of the proper amounts of each chemical. As with alum the exact amount of chemicals, lime and iron sulphate, required cannot be determined except by actual plant experience. According to the above equation the theoretical amount of lime, Ca(OH)_2 , required for each grain per gallon of ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is 0.2665 grains per gallon. Ferrous sulphate is used mainly in conjunction with sufficient lime to provide softening rather than with only enough lime for straight coagulation.

Ferric chloride, FeCl_3 , has recently been used at a number of plants. It reacts with (1) the

natural alkalinity present in water or (2) with added alkalinity as $\text{Ca}(\text{OH})_2$ as follows:

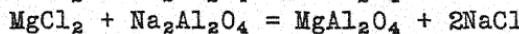
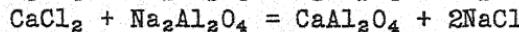
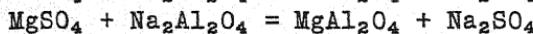
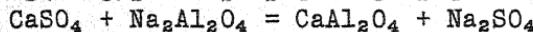
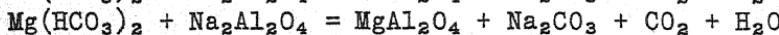
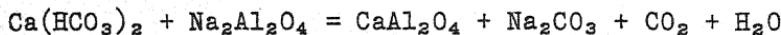


The effective coagulant is the ferric hydroxide as is the case when ferrous sulphate is used. For each grain per gallon of ferric chloride, FeCl_3 , used the theoretical amount of alkalinity required, according to above equation, is:

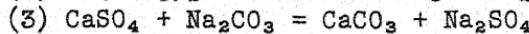
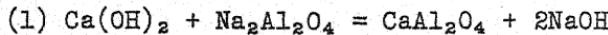
(1) Natural alkalinity, as CaCO_3 = 0.9255 grains per gallon

(2) Added alkalinity, as $\text{Ca}(\text{OH})_2$ = 0.6852 grains per gallon

Sodium aluminate, $\text{Na}_2\text{Al}_2\text{O}_4$, has been successfully used as a coagulant at some water treatment plants. It reacts with calcium and magnesium salts in water to form the aluminate of the metals. Both calcium and magnesium aluminates are effective as coagulants. The reactions follow:



When both lime and sodium aluminate are added to water the following typical reactions take place:



The aluminate of calcium in equation (1) is the effective coagulant. Equations (2) and (3) may be considered as softening reactions incidental to and accompanying the use of lime and sodium aluminate for coagulation. If softening is desired it can be most

economically secured by adding lime, $\text{Ca}(\text{OH})_2$, and soda ash, Na_2CO_3 , for the removal of the bicarbonates and sulphates respectively.

The use of chemicals in sewage treatment was widely practiced before bio-aeration processes were understood. Recently there has been a renewal of interest in the use of chemicals for sewage treatment.

Chemicals used in treatment of sewage are lime, ferrous and ferric sulphates and ferric chloride. The reactions involved are the same as those already given for water treatment. Care must be used not to add too much lime, resulting in a caustic sewage and consequent solution of suspended organic matter.

Water Hardness and Softening

Hardness of water

Hardness of water is caused principally by the elements calcium and magnesium and sometimes by iron and aluminum. Iron and aluminum are seldom present, in waters usable as water supplies, in sufficient amounts to have much significance in the hardness determinations although they are often present in sufficient quantity to cause other undesirable effects on the water supply. For this reason iron and aluminum will not be further discussed in connection with hardness and it will be assumed that hardness is caused entirely by calcium and magnesium.

Most of the calcium and magnesium is present in natural waters as bicarbonates, sulphates and sometimes as chlorides and nitrates. Hardness producing substances react with soaps forming insoluble compounds before a lather is produced. They are thus a measure of the soap consuming power of a water. They will also deposit scale when heated in boilers and hot water heating systems.

Temporary hardness is that removed by boiling. Permanent hardness is that remaining after boiling. Temporary hardness is caused principally by the presence of bicarbonates of calcium and magnesium.

Permanent hardness is due mostly to calcium sulphate which is precipitated at temperatures of above 300°F. Carbonate hardness is due to the presence of calcium and magnesium normal carbonates and bicarbonates. Non-carbonate hardness includes the calcium and magnesium sulphates, chlorides and nitrates. Sulphates are often the only non-carbonate hardness compounds present. Compounds causing permanent hardness are often termed "incrustants."

Hardness is always expressed in terms of calcium carbonate (CaCO_3). Methods of analysis and calculations used in the laboratory give results in terms of CaCO_3 . Alkalinity is also expressed in the same terms. Thus a report showing a water to have a hardness of 100 p.p.m. does not signify just what compounds cause the hardness but only that the hardness is equivalent to that produced by 100 p.p.m. of CaCO_3 .

Total hardness is most accurately found by determining the amounts of calcium and magnesium (and sometimes iron and aluminum) by a gravimetric analysis and calculating their equivalent values in terms of calcium carbonate (CaCO_3). An approximate determination of total hardness may be made with a soap solution of known strength. Total hardness may also be obtained by the soda-reagent method. This method is to be preferred to the soap method.

Carbonate hardness is found by calculation from the results of the normal carbonate and bicarbonate alkalinity determinations. If the normal carbonate and bicarbonate alkalinity, expressed in terms of CaCO_3 , is greater than the total hardness, normal carbonates or bicarbonates of sodium or potassium are present. These compounds do not cause hardness and, in this case, the carbonate hardness would be equal to the total hardness. If the sum of the normal carbonate and bicarbonate alkalinities is equal to the total hardness, the carbonate hardness is also equal to the total hardness. If the sum of the normal carbonate and bicarbonate alkalinities is less than the total hardness this sum is equal to the

carbonate hardness and the difference between this sum and the total hardness is the non-carbonate hardness.

The methods for the gravimetric determination of calcium and magnesium and equations involved in these determinations are given under "Mineral Analysis" page 16 to 18. In the calculations under the methods for making these determinations the results are obtained in p.p.m. of the elements. In order to change these to terms of hardness it is necessary to convert them to their respective equivalents of CaCO_3 and add the results. The general formulas used for this purpose are obtained from a comparison of the equivalent weights.

Solution

$$\text{Equivalent weight of } \text{CaCO}_3 = 50.05$$

$$\text{Equivalent weight of Ca} = 20.04$$

$$\text{Equivalent weight of Mg} = 12.16$$

$$(1) \text{ p.p.m. Ca} \times \frac{50.04}{20.04} = \text{p.p.m. Ca as } \text{CaCO}_3$$

$$(2) \text{ p.p.m. Mg} \times \frac{50.04}{12.16} = \text{p.p.m. Mg as } \text{CaCO}_3$$

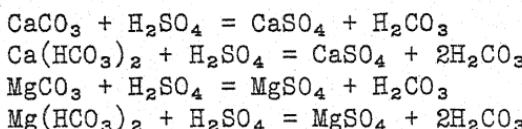
$$(3) \text{ p.p.m. Ca as } \text{CaCO}_3 + \text{p.p.m. Mg as } \text{CaCO}_3 = \text{total hardness as } \text{CaCO}_3.$$

The soap test is a rapid method for the determination of total hardness. The results obtained are only approximate. The end-point is difficult to obtain and is often unsatisfactory. Its advantage is in its rapidity and as a comparison with the results obtained by other methods.

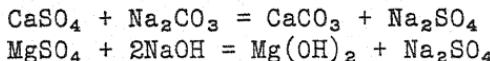
Total hardness by the soda-reagent method is also a rapid method for the determination of total hardness. Sulphuric acid is first added to decompose the normal carbonates and bicarbonates. The sample is boiled to remove carbon dioxide. The addition of the soda-reagent, a mixture of sodium hydroxide and sodium carbonate, precipitates the calcium and magnesium. The sodium hydroxide precipitates the

magnesium as magnesium hydroxide and sodium carbonate precipitates the calcium as calcium carbonate. These precipitates are filtered off and the filtrate titrated with 0.02 N sulphuric acid. A distilled water sample is treated in the same manner. The difference between the acid used for the sample and that used for the distilled water represents the hardness of the sample. The reactions are as follows:

Addition of acid to remove the carbonate hardness;



Precipitation of calcium and magnesium with soda reagent;



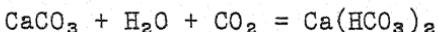
Titrating the excess soda reagent with sulphuric acid;



The solubility of the CaCO_3 formed after addition of the soda-reagent introduces a slight error. This compound is soluble to the extent of about 15 p.p.m. at ordinary temperatures. The soluble calcium carbonate will pass through the filter paper and react with the acid during the titration giving a low result. For this reason the gravimetric method of determining calcium and magnesium hardness is more accurate. However, the results obtained by the soda-reagent method are sufficiently accurate for the ordinary water treatment plant control.

Water acquires its hardness from contact with mineral bearing materials in the earth's surface. Rainfall, after reaching the earth, takes up carbon dioxide and organic acids from the soil and loses some or all of its dissolved oxygen. Limestone is

dissolved by water containing carbon dioxide, resulting in the formation of calcium bicarbonate, a soluble compound.



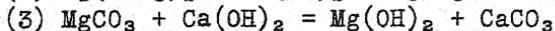
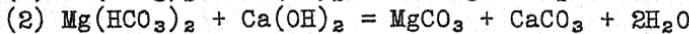
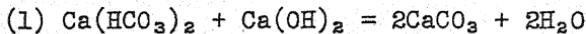
The sulphates and chlorides of calcium and magnesium are comparatively soluble and the sulphates in particular are found in appreciable quantities in many water supplies.

Water Softening

Water having less than 50-75 p.p.m. of hardness is generally considered as sufficiently soft for the ordinary uses of a public water supply. Water having 75-150 p.p.m. of hardness may be considered as moderately hard but still is not sufficiently hard to seriously interfere with its use for most purposes or to cause much public demand for water softening. Hardness above 150 p.p.m. is noticed by most persons and if the hardness is above 200 p.p.m. many homes will be provided with household softeners or cisterns.

Water for municipal purposes is most commonly softened by the lime-soda process. Lime, as $\text{Ca}(\text{OH})_2$, is used to remove the magnesium and the carbonate hardness. The lime is purchased either in the hydrate form, $\text{Ca}(\text{OH})_2$, or as the oxide, CaO , in which latter case it is slaked at the plant site to produce the hydrate. Soda ash is used to remove the non-carbonate hardness.

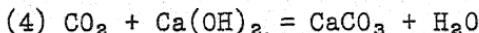
The equations expressing the reactions occurring when lime is added to remove the calcium and magnesium bicarbonates are as follows:



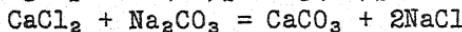
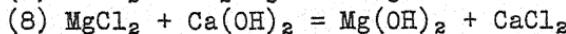
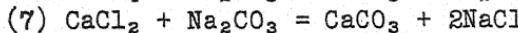
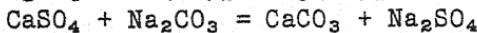
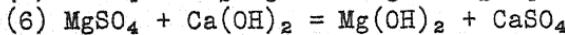
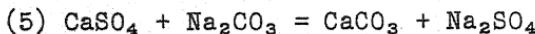
The first equation shows the reaction of calcium (as calcium bicarbonate) with lime resulting in

precipitation of the normal carbonate (CaCO_3). The removal is not complete because CaCO_3 is soluble to the extent of about 15 p.p.m. The second and third equations show the removal of magnesium by precipitating as magnesium hydroxide. If insufficient lime is added, MgCO_3 , a soluble compound, will be formed as shown in equation (2). The use of sufficient lime results in the formation of $\text{Mg}(\text{OH})_2$, an insoluble compound, as shown in equation (3). It will be noticed that twice as much lime is required for the removal of magnesium bicarbonate as for calcium bicarbonate hardness.

Lime also reacts with any free carbon dioxide present as follows:



The removal of calcium non-carbonate hardness requires the addition of soda ash (Na_2CO_3) and the removal of magnesium non-carbonate hardness requires the addition of both lime and soda ash. The following equations show the reactions involved:



In order to determine the amount of chemicals required in the lime and soda ash process of water softening it is necessary to make certain chemical tests. Methods of performing these tests are given elsewhere in this book. The tests needed are

- (1) free carbon dioxide (CO_2); (2) alkalinity;
- (3) non-carbonate (incrusted) hardness; (4) magnesium.

From the equations previously given the theoretical amounts of lime and soda ash have been calculated and are given below for use with the results

of these tests. Actual amounts of chemicals can only be determined by plant operation. Bottle experiments, paralleling the plant conditions, are useful in determining the amounts of chemicals needed.

The total lime required is equivalent to the sum of the carbon dioxide, bicarbonate alkalinity and magnesium content. The theoretical amount of lime (as CaO) required for free CO₂ is:

P.p.m. free CO₂ X 0.01062 = lbs. CaO required per 1000 gallons of water.

P.p.m. free CO₂ X 0.0743 = grains CaO required per gallon of water.

Lime (CaO) required for bicarbonate alkalinity (as CaCO₃) is:

P.p.m. bicarbonate alkalinity X 0.00467 = lbs. CaO required per 1000 gallons of water.

P.p.m. bicarbonate alkalinity X 0.0327 = grains CaO required per gallon of water.

The bicarbonate alkalinity (as CaCO₃) may be expressed as half-bound CO₂ by multiplying it by 0.44. This value of CO₂ may then be added to the free CO₂ and the amount of lime required for both CO₂ and bicarbonate alkalinity per 1000 gallons of water obtained by multiplying the sum by 0.01062.

Additional lime (CaO) required for magnesium (as Mg) is:

P.p.m. Mg X 0.01922 = lbs. CaO required per 1000 gallons of water.

P.p.m. Mg X 0.1345 = grains CaO required per gallon of water.

Since commercial quicklime is not pure CaO the amount of lime (CaO) required by above calculations should be multiplied by

$$\frac{100}{\text{per cent CaO in the quicklime used}}$$

If calcium hydrate, Ca(OH)₂, is used instead of quicklime, CaO, the amount of commercial calcium hydrate would be obtained from the above calculations by

multiplying by $\frac{100}{\text{per cent CaO in the lime hydrate used}}$. High calcium quicklime averages about 90 per cent CaO and the hydrate about 65 per cent CaO. Factors to use to obtain the theoretical amounts of pure CaO or $\text{Ca}(\text{OH})_2$ are summarized in the table below. They should be multiplied by $\frac{100}{\text{per cent purity}}$ to obtain the amount of commercial chemical required.

Item Determined in p.p.m.	Factors to multiply values in first column by to obtain required amounts of pure			
	Hydrate of lime, $\text{Ca}(\text{OH})_2$		Quicklime, CaO	
	Lbs. per 1000 gal.	Grains per gal.	Lbs. per 1000 gal.	Grains per gal.
CO ₂ (as CO ₂)	0.01403	0.09821	0.01062	0.0743
Bicarbonate alkalinity as CaCO ₃	0.006169	0.04318	0.00467	0.0327
Mg (as Mg)	0.02539	0.1777	0.01922	0.1345

Soda ash, Na₂CO₃, required to remove the non-carbonate hardness (as CaCO₃) is:

P.p.m. non-carbonate hardness X 0.0089 = lbs.

Na₂CO₃ required per 1000 gallons of water.

P.p.m. non-carbonate hardness X 0.0623 = grains of Na₂CO₃ required per gallon of water.

Illustrative problem

A water shows the following characteristics. Determine the amounts of lime and soda ash theoretically required to remove all the hardness.

Free carbon dioxide (CO_2) = 30 p.p.m. (as CO_2)

Alkalinity

with phenolphthalein = 0 p.p.m. (as CaCO_3)

with methyl orange = 270 p.p.m. (as CaCO_3)

Magnesium = 40 p.p.m. (as Mg)

Non-carbonate hardness = 60 p.p.m. (as CaCO_3)

Calculations. (Using factors from above table.)

Free CO_2

$30 \times 0.01062 = 0.32$ lbs. of CaO per 1000 gallons of water.

Alkalinity

$270 \times 0.00467 = 1.26$ lbs. of CaO per 1000 gallons of water.

Magnesium

$40 \times 0.01922 = 0.77$ lbs. of CaO per 1000 gallons of water

Total = 2.35 lbs.

If quicklime were used, containing 90 per cent water soluble CaO , the amount of quicklime required would be:

$$\frac{2.35}{0.90} = 2.61 \text{ lbs. per 1000 gallons of water.}$$

If lime hydrate were used, containing 65 per cent CaO , the amount of hydrate required would be

$$\frac{2.35}{0.65} = 3.62 \text{ lbs. per 1000 gallons of water.}$$

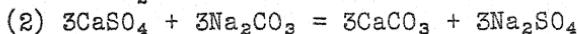
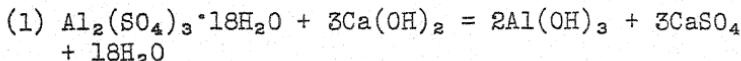
Non-carbonate hardness removal would require the following amount of soda-ash.

$60 \times 0.0089 = 0.356$ lbs. of Na_2CO_3 per 1000 gallons of water. If the soda ash were 97 per cent pure Na_2CO_3 , the amount of soda ash required would be $\frac{0.356}{0.97} = 0.367$ lbs. of soda ash per 1000 gallons

of water.

If alum was also used (to remove raw water turbidity or to assist in settling of precipitates or to assist in filtration) additional amounts of lime

and soda ash would be needed as shown in the following equations:



The amount of lime as $\text{Ca}(\text{OH})_2$ and soda ash, Na_2CO_3 , required, as calculated from the above equations are:

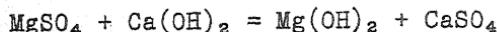
Lime, $\text{Ca}(\text{OH})_2 = 0.3335$ for each part of alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

Soda ash, $\text{Na}_2\text{CO}_3 = 0.4776$ for each part of alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

Mineral Analysis Methods

Magnesium, volumetric method

The volumetric determination of magnesium consists of adding equal volumes of limewater to distilled water and the sample respectively. The magnesium in the sample is precipitated as the insoluble hydroxide and filtered.



The amount of lime required to precipitate the magnesium in the sample is determined by titration of the distilled water and the filtered sample with 0.02 N sulphuric acid.



The difference between the ml. of acid required for the distilled water and the ml. required for the sample is used to calculate the amount of lime used in removing the magnesium. This difference X 9.72 gives the p.p.m. magnesium. The factor 9.72 is obtained as follows:

$$\text{Equivalent weight of H}_2\text{SO}_4 = 49.04$$

$$\text{Equivalent weight of Mg} = 12.16$$

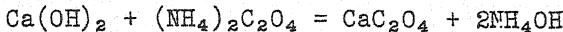
- (1) One ml. of 0.02 N H_2SO_4 contains $\frac{0.02 \times 49.04}{1000}$
 $= 0.0009808$ grams or 0.9808 mg. of H_2SO_4 .
- (2) 0.9808 mg. H_2SO_4 is equivalent to $\frac{12.16}{49.04} \times 0.9808$
 $= 0.0243$ mg. of Mg.
- (3) In the instructions for the determination of magnesium 25 ml. of the sample was used. (100 ml. diluted to 200 and 50 ml. of the diluted sample used.) Then $\frac{0.0243 \times 1000}{25} = 9.72$ mg. of Mg per liter or 9.72 p.p.m. per ml. of 0.02 N acid used.

Iron and aluminum oxides

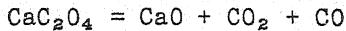
Iron and aluminum are precipitated as the hydrated oxides by ammonium hydroxide. Bromine water is added prior to the precipitation to insure the oxidation of the iron to the ferric state. The precipitation is carried out in the presence of sufficient ammonium chloride to prevent the formation of magnesium hydroxide. The combined precipitates of iron and aluminum hydrate oxides are filtered and ignited forming the oxides, Fe_2O_3 and Al_2O_3 which are weighed in that form.

Calcium, gravimetric method

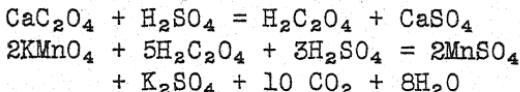
Calcium is precipitated from the water sample by the addition of ammonium oxalate after silica and iron and aluminum have been removed.



The calcium oxalate precipitate after filtering may be either ignited and weighed as the oxide (CaO)



or may be titrated with potassium permanganate.



In the first case the weight of calcium in the sample is calculated from the weight of the CaO by using the equivalent weights thus:

The equivalent weight of Ca is 20.04 and of CaO is 28.04. The weight of Ca in CaO is $\frac{20.04}{28.04} \times$ weight of CaO.

In the second case the potassium permanganate is made of such a strength that, when a 250 ml. sample is used, the ml. of permanganate $\times 10 =$ p.p.m. calcium. Each ml. of permanganate, therefore, must be equivalent to 2.5 mg. of calcium. The weight of permanganate necessary to prepare one liter of such a solution is calculated by the use of the equivalent weights.

Solution

$$\text{Equivalent weight of KMnO}_4 = 31.60$$

$$\text{Equivalent weight of Ca} = 20.04$$

$$\frac{31.60}{20.04} \times 2.5 = 3.94 \text{ mg. of KMnO}_4 \text{ per ml. required}$$

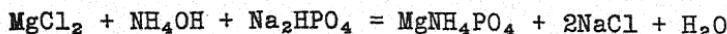
$$= 3.94 \text{ grams per liter.}$$

The normality of such a solution is calculated thus:

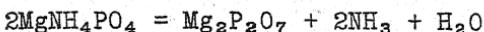
$$\frac{3.94}{31.6} = 0.1246 \text{ N.}$$

Magnesium, gravimetric method

Silica, iron and aluminum, and calcium must be removed from the sample before magnesium is determined. The magnesium is precipitated as magnesium ammonium phosphate, (MgNH_4PO_4).



This precipitate is filtered and ignited to magnesium pyrophosphate, ($\text{Mg}_2\text{P}_2\text{O}_7$) in which form it is weighed.



In order to calculate the magnesium in the pyrophosphate the equivalent weights are again used.

Solution

$$\text{Equivalent weight of Mg}_2\text{P}_2\text{O}_7 = 55.67$$

$$\text{Equivalent weight of Mg} = 12.16$$

(1) The weight of $\text{Mg}_2\text{P}_2\text{O}_7$ X $\frac{12.16}{55.67}$ = grams of Mg in sample.

(2) To convert this weight to p.p.m.

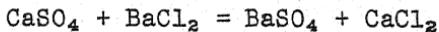
Grams X 1000 = mg. per sample. If a 250 ml. sample is used, Mg X 4 = mg. per liter or p.p.m.

Combining the above steps, the general formula is obtained:

$$\text{Weight of Mg}_2\text{P}_2\text{O}_7 \text{ (grams)} \times 873.6 = \text{p.p.m. Mg.}$$

Sulphate, gravimetric method

Sulphates are determined by precipitating with barium chloride and filtering, igniting and weighing the precipitate, barium sulphate.



To calculate the weight of sulphate in the barium sulphate precipitate, the equivalent weights are used.

Solution

$$\text{Equivalent weight of BaSO}_4 = 116.71$$

$$\text{Equivalent weight of SO}_4 = 48.03$$

(1) Weight of BaSO_4 (grams) X $\frac{48.03}{116.71}$ = grams of SO_4 in sample.

(2) To convert this weight to p.p.m. Grams X 1000 = mg. per sample. If a 250 ml. sample is used, the mg. per sample X 4 = mg. per liter or p.p.m.

Combining the above steps gives a general formula, Weight of BaSO_4 (grams) X 1646.1 = p.p.m. SO_4 .

Sodium and potassium, gravimetric method

Sodium and potassium are converted into their chlorides and weighed as such. These chlorides, are very soluble and in order to obtain them free from other compounds, all of the other metals and negative radicals must be removed from the sample. When this is accomplished the residue of the sodium and potassium chlorides, after the evaporation of the water, is weighed and the results expressed in terms of sodium.

In order to convert the weight of sodium and potassium chloride to sodium it is necessary to assume that the entire weight is sodium chloride and use the equivalent weights as follows.

Solution

$$\text{Equivalent weight of NaCl} = 58.46$$

$$\text{Equivalent weight of Na} = 23.00$$

$$(1) \text{Weight of NaCl (grams)} \times \frac{23.00}{58.46} = \text{grams Na in sample.}$$

$$(2) \text{Grams Na in sample} \times 1000 = \text{mg. per sample.}$$

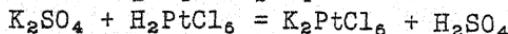
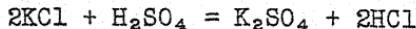
$$(3) \text{If 250 ml. sample is used, mg. per sample} \times 4 \\ = \text{mg. per liter or p.p.m.}$$

Combining the above steps the general formula is obtained.

$$\text{Grams NaCl} \times 1573.6 = \text{p.p.m. Na.}$$

Potassium

In order to distinguish between sodium and potassium in a sample, the potassium is precipitated from the combined chlorides with platinic chloride.



The potassium chloroplatinate precipitate (K_2PtCl_6) is filtered, ignited and weighed. In order to obtain the weight of potassium chloride from the weight of the precipitate the equivalent weights are used.

Solution

Equivalent weight of K_2PtCl_6 = 243.10

Equivalent weight of KCl = 74.56

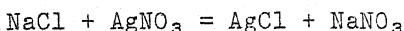
Equivalent weight of K = 39.10

Weight of K_2PtCl_6 (grams) $\times \frac{74.56}{243.10}$ = grams KCl
in sample.

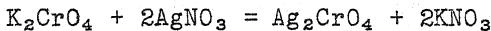
Grams KCl in sample $\times \frac{39.10}{74.56}$ = grams K in sample.

Chloride, volumetric method

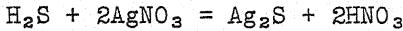
In this procedure the chloride of the sample is determined by titration with a standard silver nitrate solution in the presence of potassium chromate indicator. The chloride is precipitated as silver chloride (a white precipitate).



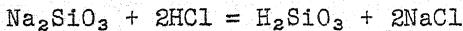
The end-point of the titration is reached when a brown precipitate of silver chromate first appears due to the reaction of a slight excess of silver nitrate with the potassium chromate.



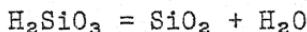
A correction of 0.2 ml. is made for the excess silver nitrate required to produce a noticeable amount of brown precipitate. Hydrogen sulphide interferes with the reaction precipitating black silver sulphide.

Silica

Silica occurs in water in the form of very finely divided clay particles and of silicates in colloidal solution. These compounds upon being acidified produce the silicic acids.



The acids upon drying and ignition are dehydrated producing silica.

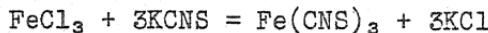


Total and residual iron

Iron may be present in two forms, namely the reduced form (ferrous) and the fully oxidized form (ferric). Ferric iron is seldom found in true solution in natural waters, unless they are highly acid, because of the formation of insoluble ferric oxide hydrates. These hydrates occur in colloidal solution in many cases.

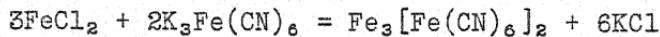
Ferrous salts are more likely to be found in true solution although they are easily oxidized to the ferric state and precipitated in alkaline waters as the hydrated oxides. Ferrous iron has a positive valence of two while ferric has three.

Ferric iron is determined by producing a red colored iron compound, ferric thiocyanate by the addition of potassium thiocyanate.



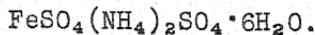
The red color produced is compared with color standards.

Ferrous iron is also determined colorimetrically by producing a blue compound, known as Turnbull's blue, by the addition of potassium ferricyanate.



The quantity of ferrous iron is determined by comparison with the color produced by known amounts of ferrous compounds treated in a similar manner.

Both of the standard iron solutions are prepared from ferrous ammonium sulphate crystals,



The weight of this compound necessary to prepare a solution containing 0.1 mg. of iron per ml. is calculated as follows:

Solution

Equivalent weight of ferrous ammonium sulphate crystals = 196.07

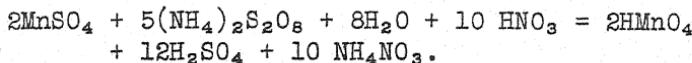
Equivalent weight of ferrous iron = 27.92

(1) 0.1 mg. per ml. = 0.1 gm. per liter

(2) $0.1 \times \frac{196.07}{27.92} = 0.7023$ gms. ferrous ammonium sulphate crystals per liter.

Manganese, colorimetric

Manganese is determined by oxidation of the managanous compounds to permanganate and a comparison of the color produced with standard managanous sulphate solutions treated in a similar manner.



The standard managanous sulphate solution is prepared by reducing, with oxalic acid, the necessary amount of potassium permanganate to make 1 liter of solution so that 1 ml. = 0.1 mg. Mn. The amount of permanganate necessary is determined as follows.

Solution

Molecular weight of KMnO_4 = 158.03

Atomic weight of Mn = 54.93

(1) 0.1 mg. per ml. = 0.1 gm. per liter.

(2) $0.1 \times \frac{158.03}{54.93} = 0.2877$ gm. KMnO_4 .

Residual alum, colorimetric method

The logwood test for the presence of residual alum in filtered water has been used as a qualitative test for many years. The alizarin red S test given in this manual has many advantages over the logwood

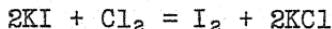
test, one being its adaption as a quantitative procedure.

The test makes use of the formation of a colored compound by the reaction of aluminum with the dye. This color is compared with that of a standard alum solution treated in the same manner. The stock alum solution is prepared by dissolving an approximate amount of aluminum sulphate crystals, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, in water and standardizing by a gravimetric analysis for aluminum. The method used is similar to that used for the iron and aluminum oxides determination. This stock solution is then diluted so that 1 ml. = 0.01 mg. Al_2O_3 .

Chlorine Determination

Chlorination of water and sewage for sterilization and of sewage for odor control and reduction of biochemical oxygen demand is being practiced in many treatment plants. To be effective for sterilization, sufficient chlorine must be added to satisfy the chlorine demand and to leave residual chlorine after a contact period.

There are a number of methods used for the chlorine demand determination. The one given in this manual is simple and sufficiently accurate for the majority of purposes. It depends upon the liberation of iodine from potassium iodide by free chlorine.



The presence of the iodine is shown by the formation of a blue starch-iodide compound.

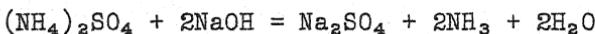
Residual chlorine by the o-tolidine method is subject to interference by nitrites and iron, causing high results or even indicating a chlorine content where none is present. The test, however, is in general use and if the procedure given in this manual is carefully followed, will give satisfactory results.

Nitrogen Determinations

Organic nitrogen

The organic nitrogen determination is a measure of the nitrogen in the form of proteins or intermediate decomposition products. The ammonia nitrogen is first removed by boiling from a slightly alkaline solution. Ammonia can be volatilized from an alkaline medium, but not from a strong acid.

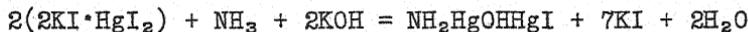
After the removal of ammonia, concentrated sulphuric acid is added and the water distilled off. The heating is continued until the organic compounds have been completely decomposed by the hot acid, at which time the nitrogen will have been entirely converted to ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$. The ammonia is liberated by making the solution alkaline with sodium hydroxide.



The solution is then distilled and the distillate containing the ammonia collected and analyzed for ammonia nitrogen.

Ammonia nitrogen

The ammonia nitrogen determination depends upon a comparison of colors produced when the sample and standards are treated with Nessler's reagent. Nessler's reagent ($2\text{KI}\cdot\text{HgI}_2$) reacts with the ammonia in alkaline solution giving a yellow colored compound.

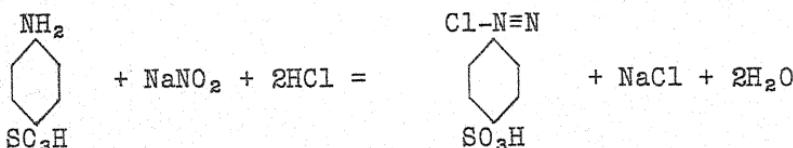


In order to free the solution from interfering substances it must be either clarified by coagulation with copper sulphate, $\text{CuSO}_4 + 2\text{NaOH} = \text{Cu}(\text{OH})_2 + \text{Na}_2\text{SO}_4$ or by distillation.

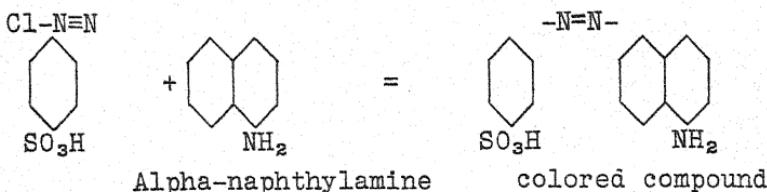
Nitrite nitrogen

The nitrite determination is made by comparing colors produced by treating the sample and standards

with sulphanilic acid and alpha-naphthylamine hydrochloride. The resulting red color is due to the production of azobenzol-naphthylamine sulphonic acid. The reactions are represented by the following equations:

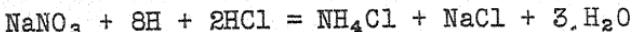


Sulphanilic acid

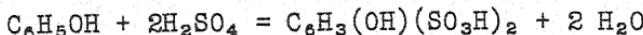


Nitrate nitrogen

The nitrates are the final oxidation products of the organic nitrogen compounds. They may be determined in two ways: (1) By reducing them to ammonia with nascent hydrogen. The reduction takes place in a hydrochloric acid solution which immediately converts the ammonia to ammonium chloride.

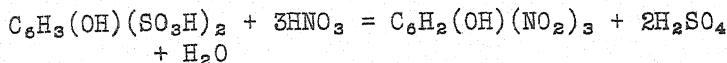


The ammonia is then determined by the ammonia nitrogen method and converted to terms of nitrate nitrogen. (2) By the disulphonic acid method. Disulphonic acid is prepared by treating phenol with sulphuric acid.



When nitrates are treated with disulphonic acid and

the resulting solution made alkaline with sodium hydroxide a yellow compound is produced. The compound is the sodium salt of picric acid formed by the nitration of the phenol.



The color produced by this compound in the sample is compared with potassium nitrate standards treated in a similar manner.

Oxygen Determinations

Oxygen consumed

The oxygen consumed determination is a measure of the amount of oxygen required to oxidize unstable materials in a sample by means of potassium permanganate in an acid solution. This test has been largely replaced by the biochemical oxygen demand determination since it does not give results which are comparable to those obtained from biological oxidation processes which occur in nature. The test has one advantage in that the results can be obtained in less than one hour while the biochemical test requires, at least, five days. Due to the fact that potassium permanganate is selective in its reaction and attacks the carbonaceous and not the nitrogenous matter the results will be lower than those obtained by the biochemical oxygen demand method.

Two standard solutions are required, potassium permanganate and ammonium oxalate. The preparation of stock standard solutions from which these standards can be prepared by dilution is discussed in Section II, pages 94 and 95. The standard solutions are prepared in such a manner that 1 ml. = 0.1 mg. of oxygen. (1 liter = 0.1 gram.) The normality of the solution to fulfill this condition may be determined as follows:

$$\text{Normality} = \frac{\text{grams oxygen per liter}}{\text{equivalent weight of oxygen}} = \frac{0.1}{8.0}$$
$$= 0.0125 \text{ N.}$$

The stock standard solutions may be diluted to this normality using the quantity of stock solution as determined by the formula $\frac{1000 \times 0.0125}{\text{normality of stock solution}}$
= ml. of stock solution required per 1 liter of 0.0125 N standard solution.

The 0.0125 N standard ammonium oxalate solution may also be prepared by direct weight according to the directions in Section II, page 106. The weight of ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, required to make one liter of a solution, one ml. of which is equal to one mg. oxygen, may be calculated as follows:

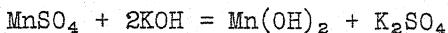
Equivalent weight of crystalline ammonium oxalate = 71.05.

A 0.0125 N solution of ammonium oxalate will contain $71.05 \times 0.0125 = 0.8881$ grams crystalline ammonium oxalate per liter.

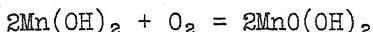
Dissolved oxygen, Winkler method

The Winkler method may be used for the determination of dissolved oxygen in the majority of cases encountered in the water and sewage plant laboratory. In some cases errors may be introduced by the presence of nitrites, iron salts, and certain organic compounds. The effect of nitrites can be minimized by careful manipulation of the procedure as will be shown later. In cases where the interfering compounds are present in sufficient quantities to cause a significant error, the Rideal-Stewart modification must be used.

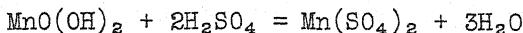
The reaction involved in the various steps of the Winkler method are represented by the following equations: Manganese sulphate reacts with the potassium hydroxide in the alkaline potassium iodide mixture to produce a white flocculent precipitate of manganese hydroxide:



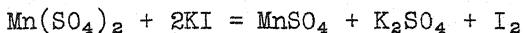
If the white precipitate is obtained, there was no dissolved oxygen in the sample and there is no need to proceed further. A brown precipitate shows that oxygen was present and reacted with the manganous hydroxide. The brown precipitate is manganic basic oxide:



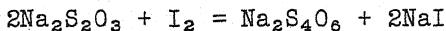
Upon the addition of the acid, this precipitate is dissolved forming manganic sulphate.



There is an immediate reaction between this compound and the potassium iodide previously added, liberating iodine and resulting in the typical iodine coloration of the water.



The quantity of iodine liberated by these reactions is equivalent to the quantity of oxygen present in the sample. The quantity of iodine is determined by titrating a portion of the solution with a standard solution of sodium thiosulphate:



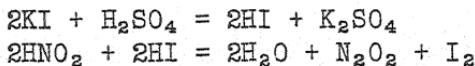
The thiosulphate is made of such a strength that 1 ml. = 0.2 mg. of oxygen. Such a solution would have a normality obtained as follows:

- (1) 0.2 mg. per ml. = 0.2 gms. per liter
- (2) Equivalent weight of oxygen = 8.0

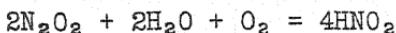
$$\frac{0.2}{8.0} = 0.025 \text{ N}$$

The preparation of the stock standard solution from which this standard may be prepared has already been discussed on page 94.

The error due to nitrites is introduced at the time the solution is made acid with sulphuric acid. In an acid medium, nitrites react with the potassium iodide liberating iodine.



If the reaction was complete at this point, the error due to nitrites in most cases would not be significant. However, if the sample is allowed to stand exposed to the air, the oxygen which dissolves will react with the N_2O_2 again producing the nitrite.



This will again liberate more iodine. Should this cycle be repeated a sufficient number of times, the error introduced would soon become very large. The continuous reaction can be minimized by an immediate and rapid titration of the sample after it is exposed to the air.

In the Rideal-Stewart modification, the nitrites, iron and organic matter are first oxidized by potassium permanganate and excess permanganate removed with potassium oxalate. Care must be taken not to add too great an excess of the oxalate or an error will be introduced in the final result.

Biochemical Oxygen Demand

The biochemical oxygen demand determination is a measure of the oxygen required to oxidize the organic matter in a sample, through the agency of microscopic organisms (bacteria). The test consists of the determination of dissolved oxygen prior to and following a period of incubation at 20° Centigrade. The incubation period is usually five days.

If the oxygen demand of the sample is greater than the available dissolved oxygen, a dilution is made. The amount of dilution depends upon the oxygen demand and must be such that an appreciable amount of dissolved oxygen (1.5 to 2.0 p.p.m. minimum) remains after the incubation period. For wastes or sewage having an unknown oxygen demand, it is necessary to make up a number of dilutions in order to be sure that one will meet the requirements.

There are a number of factors which influence the rate of oxidation of organic matter by bacteria and hence, the 5-day oxygen demand. The type of diluting water, pH and bacterial content are the most important. The diluting water prepared according to Section II, page 108 has been temporarily accepted as a standard diluting water. The optimum pH is between 7.0 and 7.6 and under special conditions the pH may require adjustment prior to incubation. Sterilized sewage effluents or samples not containing a bacterial flora must be seeded with bacteria before incubation. It is apparent that directions cannot be given which will cover all special conditions encountered in making this test. The methods given will meet the majority of situations and the laboratory worker must be able to adopt such modifications as to meet the special requirements.

Some samples of water and sewage have an immediate oxygen demand and it is sometimes desirable to know the quantity of this immediate demand. The demand is due to the presence of easily oxidizable substances such as hydrogen sulphide, iron, etc., substances which are encountered for instance, in a septic sewage. Such a condition, of course, could only exist in samples entirely devoid of oxygen.

The immediate oxygen demand may be determined from two dissolved oxygen determinations, one made on diluting water and the other on a dilution of the waste or sewage with the diluting water. This dilution must be of such strength that there will be an appreciable amount of oxygen remaining after mixing.

The test on the dilution is made immediately following mixing. The initial demand is calculated as follows:

P.p.m. D.O. diluting water X per cent diluting
water in dilution

$$(1) \frac{100}{}$$

= p.p.m. D.O. of the dilution before any immediate demand is exerted. Let this value = A.

(2) P.p.m. D.O. of dilution after mixing = B.

$$(3) \text{Then } (A - B) \times \frac{100}{\text{per cent sample in dilution}} = \text{p.p.m. immediate oxygen demand.}$$

The 5-day biochemical oxygen demand does not represent the total demand of the sample for oxygen. Sometimes the total demand is desired. This can be calculated from the following table which represents the per cent of the total oxygen demand satisfied at various periods of incubation of the sample.

The values given in this table apply to sewage, water and industrial wastes in a medium favorable for the growth and activity of the bacteria responsible for the oxidation of the organic matter. This must be borne in mind and allowance made for conditions which tend to interfere with the proper reaction. For instance, in the oxidation of some trade wastes there is a decided lag in the rate of oxidation due to unfavorable conditions. Or there may be a large initial or immediate demand which would not conform to the rate indicated.

The values given in the table are usually known as the "Relative stability numbers." Relative stability is also a measure of oxygen demand except that the values obtained are relative and not absolute. This test makes use of the fact that methylene blue is decolorized if no oxygen is available. A sample treated with methylene blue will remain colored as long as oxygen is present. At the time when the oxygen demand has removed the oxygen a certain per cent of the demand is satisfied. This per cent is that

Rate of Biochemical Oxidation			
Period of incubation at 20°C. (days)	Per cent of demand satisfied	Period of incubation at 20°C. (days)	Per cent demand satisfied
0.5	11	8.0	84
1.0	21	9.0	87
2.0	37	10.0	90
3.0	50	12.0	94
4.0	60	14.0	96
5.0	68	16.0	97
6.0	75	20.0	99
7.0	80		

given in the above table. For instance, if a sample remains colored for 5 days there was originally sufficient dissolved oxygen in the sample to satisfy 68 per cent of the total oxygen demand.

To calculate the oxygen demand at any period from the biochemical oxygen demand (B.O.D.) determination the following method may be used:

Let A = p.p.m. B.O.D. as determined.

Let B = per cent demand satisfied in the period used as obtained from above table.

Let C = per cent demand satisfied in the period desired as obtained from above table.

$$\frac{A}{B} \times C = \text{p.p.m. B.O.D. for period desired.}$$

Example

The 5-day B.O.D. of a sample is found to be 140 p.p.m. What is the 10-day B.O.D.?

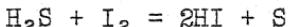
Solution

$$A = 140; B = 68; \text{ and } C = 90.$$

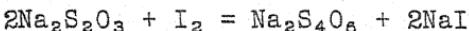
$$\frac{140}{68} \times 90 = 185 \text{ p.p.m. 10-day B.O.D.}$$

Hydrogen Sulphide

Hydrogen sulphide is determined by its reducing action on a standard iodine solution. The reaction is represented by the following equation:



Since it is not feasible to titrate the sulphide directly, more than the required amount of the iodine solution is added and the excess determined by titration with sodium thiosulphate standard.



The iodine solution is prepared by dissolving iodine in a solution of potassium iodide. The presence of the iodide increases the solubility of the iodine. The solution is standardized against 0.025 N sodium thiosulphate and adjusted to be equivalent to that solution.

The strength of the 0.025 N iodine solution in terms of hydrogen sulphide is determined as follows:

$$\text{Equivalent weight H}_2\text{S} = 17.05.$$

$$1 \text{ liter of } 0.025 \text{ N iodine solution} = 17.05$$

$$\times 0.025 = 0.426 \text{ grams H}_2\text{S}.$$

$$1 \text{ ml. of } 0.025 \text{ N iodine solution} = 0.426 \text{ mg.}$$

$$\text{H}_2\text{S}.$$

Sewage Sludge

Fertilizer value

The value of sewage sludge (digested primary sludge) as a fertilizer is low when compared with commercial fertilizers. It has an especially high value as a soil conditioner. Its use as a fertilizer and soil conditioner provides the most satisfactory means of disposal.

This discussion is not concerned with the value

of the sludge as a fertilizer, but is concerned with the methods of analysis of the sludge for its fertilizer constituents. The analysis consists of a determination of moisture, humus, phosphoric acid (P_2O_5), nitrogen, and potash. The latter is often omitted since the potash content is consistently low and the determination complicated and time consuming.

The results of a fertilizer analysis are always based on the dry weight of the material, except the moisture determination which is based on the weight of the sample collected.

As in all other determinations the accuracy of the results depends in a large measure on proper sampling. A discussion of sampling of sludge for fertilizer analysis is given in the Appendix, page 174.

The following table gives the limits within which the quantities of the various constituents will probably lie for both activated and digested sludges.

Limits of Fertilizer Values in Sewage Sludges
(Values are per cents on dry basis)

Activated sludge Digested sludge

Phosphoric acid (P_2O_5)	1.5-3.0	1.0-3.0
Nitrogen (N)	3.5-5.5	1.5-3.5
Potash (K)	0.2-0.3	0.1-0.3
Humus	60-70	25-35

Loss on ignition and humus

The loss on ignition determination is not a true measure of the organic matter (humus) in a sludge because of the decomposition of inorganic salts, carbonates in particular, at the temperatures used. Almost every method calls for the ignition at "low red heat", which is a variable temperature depending upon the opinion of the worker as to what constitutes a "low red" color. The following table gives the

temperatures and corresponding colors of heated bodies.

Temperature of Glowing Bodies

Color	Temperature	
	Degrees Centigrade	Degrees Fahrenheit
First visible red	525	980
Dull red (low red)	700	1292
Turning to cherry	800	1472
Cherry proper	900	1652
Bright cherry	1000	1892
Dull orange	1100	2012
Bright orange	1200	2192
White	1300	2632

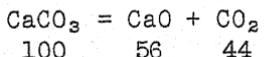
Calcium carbonate is the principal carbonate in sewage sludge. This carbonate is either present originally in the sludge or is produced by the partial ignition of certain calcium organic salts. Although the temperature at which calcium carbonate decomposes is given as 825°C., yet there is evidence that partial decomposition takes place at much lower temperatures. This being the case, a variable partial decomposition may take place at 700°C. (low red heat) and a much greater decomposition at temperatures approaching 825°C.

The results of ignition at low red heat are subject to considerable error if the values are to be interpreted in terms of humus. This temperature is, however, required to assure the complete combustion of the carbon.

In order to obtain a more accurate value for humus in fertilizer, temperatures of ignition should be such as to insure a complete decomposition of the calcium carbonate and a correction then made. This procedure does not take into account other minor

losses which may occur due to the presence of other mineral salts. Most of the other salts which might be present are soluble compounds and would be largely removed with the sludge liquor, sludge beds or filters. The amount of these salts present in most cases would be too small to have much significance.

The decomposition of calcium carbonate takes place according to the following equation:



The figures below the formulas in the above equation are the molecular weights. Thus, 44 parts in 100 or 44 per cent of the calcium carbonate is liberated as carbon dioxide gas during ignition.

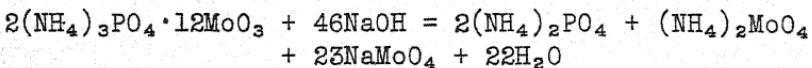
The correction may be appreciable in some cases and of little significance in others. The calcium carbonate content of digested primary sludge varies from 5 to 12 per cent of the weight of the dried sludge. In activated sludge, since the calcium carbonate content is seldom over 1 to 2 per cent, the correction need not be made, in which case the loss on ignition may be reported as humus.

In the determination of calcium the same procedure is used as that recommended for the determination of calcium in water. This method is discussed on page 147.

Phosphoric acid anhydride (P_2O_5)

Phosphates present are reported as their equivalents in terms of P_2O_5 . In the phosphate determination, the organic matter in the dried sludge is first decomposed with sulphuric acid. After adjusting the solution to neutrality with nitric acid and ammonium hydroxide, the phosphate is precipitated with ammonium molybdate. The precipitate is ammonium phospho-molybdate, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$.

This precipitate is dissolved in an excess of 0.3238 N sodium hydroxide solution:



The excess of the 0.3238 N hydroxide used is determined by titration with 0.3238 N hydrochloric acid. The difference between the quantities used in the titration represents the amount of the hydroxide required to react in the above equation.

The 0.3238 N acid and alkali are used because 1 ml. of alkali having this normality is equivalent to 1 mg. of P_2O_5 , thus simplifying the calculations.

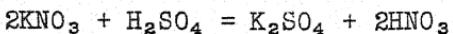
This value for the normality of the alkali can be obtained by consideration of the above equation. It will be seen that 2 molecules of ammonium phospho-molybdate reacts with 46 molecules of sodium hydroxide. The 2 molecules of ammonium phospho-molybdate contain 2 atoms of phosphorus from which it follows that 2 atoms of phosphorus in the above equation are equivalent to 46 molecules of sodium hydroxide. Since this is true one molecule of P_2O_5 is equivalent to 46 molecules of NaOH and the equivalent weight of P_2O_5 is its molecular weight divided by 46 or

$$\frac{142.1}{46} = 3.09. \text{ At } 1 \text{ N solution will, therefore, be}$$

equivalent to 3.09 grams P_2O_5 per liter or 3.09 mg. per ml. and a 0.3238 N solution will be equivalent to $3.09 \times 0.3238 = 1 \text{ mg. P}_2\text{O}_5 \text{ per ml.}$

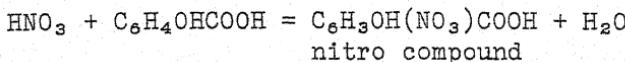
Nitrogen

The nitrogen determination consists of first decomposing the sludge with a mixture of salicylic and sulphuric acids. The salicylic acid is added to prevent the loss of nitrogen as nitrates since it has been found that nitrates are almost entirely decomposed by heating with sulphuric acid alone as follows:

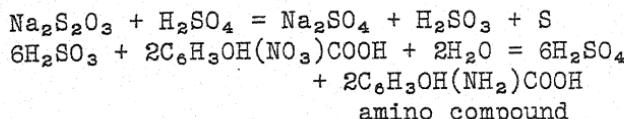


The HNO_3 is volatile. Salicylic acid retains the

nitrates in the form of the nitro compound:

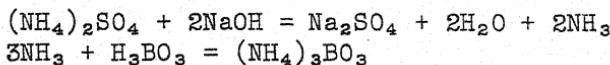


Sodium thiosulphate is then added to reduce the nitro compound to an amino compound which is then broken down into ammonia.

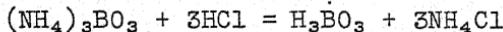


All nitrogen compounds are then reduced to ammonium sulphate by sulphuric acid. Potassium sulphate crystals are added to increase the boiling temperature of the acid and insure a complete break-down of the organic matter.

After the digestion is complete the solution is made alkaline and the ammonia distilled into boric acid.



The amount of ammonia, all of which has reacted with the boric acid, is determined by titration with 0.5 N hydrochloric acid.



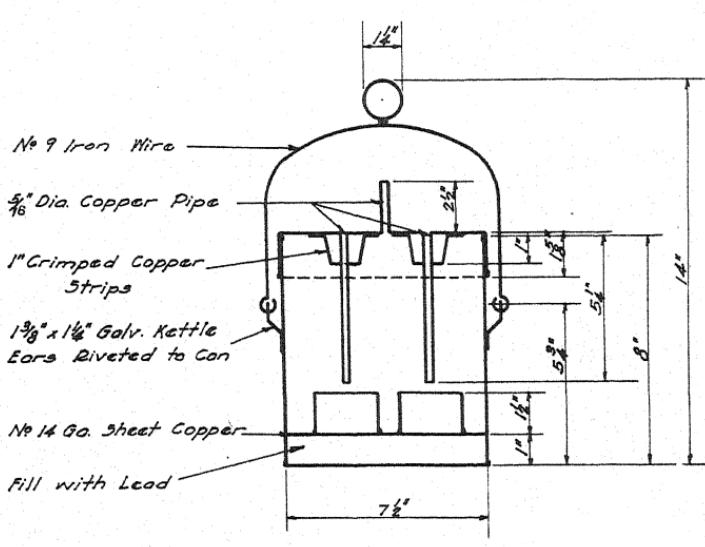
The amount of nitrogen equivalent to 1 ml. of the 0.5 N acid is determined as follows:

Equivalent weight of N = 14.

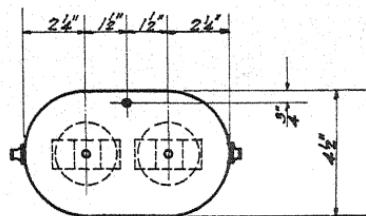
1 liter of 0.5 N acid is equivalent to $14 \times 0.5 = 7.0$ grams N or 1 ml. is equivalent to 7.0 mg. N.

Potash

The method for the determination of potash is discussed under the sodium and potassium determination page 150.



SECTION



NOTE :-

Make Can of 14 Gauge
Copper Stock. Solder all
Joints, Crimp all Edges.
Solder Tubing to Can and
Braces

PLAN

SAMPLING DEVICE
FOR
DISSOLVED OXYGEN SAMPLES

APPENDIX

Sampling

Sampling of a water, sewage or trade waste, must be accomplished with proper precautions to secure a representative sample. Too often the error in sampling is inconsistent with the accuracy of the determinations made in the laboratory. It is seldom sufficient to rely on the results of a single ("grab") sample. It is more often necessary to use a composite sample made up of a number of individual samples or to use the results of analyses of a number of individual or composite samples. Good judgment must be used in any case in selecting the sampling method to be used, the selection of the method often being influenced by the laboratory facilities available. It is evident that the results of a laboratory analysis, however accurate that analysis may be, cannot represent an accuracy for the material sampled of a greater degree than the accuracy with which the sample was taken.

In the collection of representative samples, the following points must be taken into consideration:

- (1) The character of the laboratory examinations to be made.
- (2) The use to be made of the results of the analysis.
- (3) The character of the material sampled and the variation in character over the period of sampling.
- (4) The variation in the rate of flow over the period of sampling.

Samples for the ordinary chemical analysis of water and sewage should be collected in clean glass-stoppered bottles. The size of the sample collected depends upon the analysis to be made.

Well water samples

Well waters are usually quite constant in character and composite sampling is not necessary in order to obtain representative samples. Before the sample is taken the well should be pumped for some time so that the sample will represent the ground water from which the well is fed. The container must be rinsed with the water and then completely filled. If an analysis is to be made for dissolved gases, carbon dioxide and oxygen, this analysis should be made immediately.

Ponds and lakes

Ponds and lakes are often subject to variable conditions resulting from natural causes, such as seasonal turnovers, rains and winds. This variation is usually not as rapid nor over such a wide range as is encountered in a flowing body of water. Single samples are often sufficiently representative in these cases, but they should be taken often enough to take into account those variations which are likely to occur.

Flowing streams

Flowing streams are subject to considerable variation and in most cases require composite sampling or the averaging of the results of the analyses of a large number of samples. Samples from a stream should be taken at a point which most nearly represents the conditions in the stream. This point should be within the flowing channel and at a depth about one-third of the way from the bottom. Wide, deep streams may require the collection of samples in a number of verticals across the stream and at several depths in the verticals in order to obtain a representative sample. Composite samples made up of hourly individual samples taken according to flow are usually considered as representative of the stream condition.

Water treatment plants

In water treatment plant control, individual samples or composites over short periods of time, must be taken at frequent enough intervals and at such points in the treatment process so as to determine the quantity of chemicals required and the accomplishments obtained. The exact schedule will vary with the particular conditions at each plant. For instance, a raw water supply from wells may require but one sample a day, while a supply from a stream may require hourly sampling. Many laboratories have provisions for taking of constant samples at all points in the process, the particular water being piped to the laboratory.

Sewage and sewage treatment plants

In sampling influents and effluents from sewage treatment plants or sewage from a sewerage system it is particularly important to take composite samples. The character of sewage is too variable in short intervals of time to place any reliance upon individual samples. Composite samples should be made up of individual samples which vary in size according to the relative flows at the time they are taken.

It is desirable to extend the taking of the composite over a 24-hour period, or in smaller plants, at least over several hours. A better study of plant accomplishments may be made by dividing the 24 hours into two or more groups and obtaining a composite for each group.

Sewage samples may be readily collected by means of dippers or cans several inches in diameter. The dipper should be immersed well into the sewage and the sample taken as near as possible to a point one-third of the distance from the bottom of the channel or sewer. The dippers may be made of various sizes to conform to the flows obtained. Each individual sample should be deposited in a larger receptacle of sufficient size to hold the composite. The composite should be kept at a low temperature in order to

inhibit bacterial action and prevent as much change in character as is possible.

Trade wastes

The methods for sampling trade wastes must be suited to the particular waste. If the rate of flow and character of the liquid are both variable, the procedure should be similar to that used for sewage. In some cases the flow and character are constant requiring only an individual sample. Often there are times of periodic or occasional discharges of strong wastes. An inspection of the trade processes should be made before any samples are taken in an endeavor to ascertain the methods of waste discharge.

Sampling for dissolved oxygen

It is necessary to make dissolved oxygen determinations on samples at the time of collection. This makes necessary the use of individual samples for this test. Samples should be taken with extreme care so as to avoid contact of the sample with air. In order to facilitate the taking of dissolved oxygen samples, a sampling can similar to that shown in Figure 1 may be used. This can should be of such a size that the displacement in the can is at least four times that of the sample bottle or bottles. The use of this can prevents contact of the sample with air. The can shown with provision for two bottles is convenient for the taking of stream survey samples because it is often desired to use one bottle for an immediate dissolved oxygen test and the other bottle for a biochemical oxygen demand test.

Sampling of sewage sludge

Samples of wet sludge being drawn from a tank should be composited from individual samples. A regular schedule should be adopted for individual collections at various times during the drawing operation. Ten minute intervals are often used. The individual samples should be placed in a large

receptacle, well mixed and a smaller sample taken for the laboratory.

If sludge from a drying bed is to be sampled, a composite should be made up by taking individual samples from various parts of the bed. The bed should be divided into a number of sections and individual samples taken from the full depth of the material in each section. This may be done by forcing a 1 inch thin-walled metal tube into the sludge the full depth, withdrawing the tube and removing the adhering sand. A plunger placed in the tube will facilitate the removal of the sample. All of the individual samples should be well mixed and ground together. The final sample for analysis should be obtained by quartering the composite. Quartering consists of dividing the pile on the paper into quarters, discarding opposite quarters, again mixing, quartering and discarding until the required size is obtained.

Sampling of dry material

Samples of lime, soda ash, alum, dried sewage sludge, filter sand, etc., must be taken in such a manner as to be representative of the entire mass from which they are taken. Individual samples, taken from various locations in the material, should be composited. This composite should be dried and ground, if necessary, to the degree of fineness required for the analysis. The sample should then be thoroughly mixed. This may be done conveniently by placing it on a large sheet of paper and by raising alternate corners, rolling the material diagonally across the paper. If the sample is too large for analysis it must be divided by quartering.

Use and Care of Laboratory Equipment

The analytical balance

The analytical balance is the most important piece of equipment in the laboratory and should be

treated accordingly. The following directions must be carefully followed if correct weights are to be obtained and the sensitivity of the balance used to its fullest extent.

Before using, clean the balance floor and pans with a camel's-hair brush. While not in use raise the balance beam and pans from their knife-edge supports by means of the milled knob outside of the balance case. Also raise the pan rests against the pans by means of the knob for that purpose. After cleaning, lower the balance beam and pans slowly to their knife-edge supports. Release the pan rests and notice if the pointer swings equal distances on each side of the zero of the scale. If it does not swing equal distances (within less than one division) it may be adjusted by the adjusting screws or the mean position of the swings may be determined and used as the zero point.

With the balance beam and pans lifted from their knife-edge supports and the pan rests against the pans, place the object to be weighed in the left-hand pan and release the pan rests. If the pans swing at any time they may be stopped by lowering and raising the pan rests. Place a weight in the right-hand pan which you judge is just heavier than the object being weighed. Lower the beam support slowly. If the weight is too light (pointer moves to right) raise the beam support and replace the weight with the next heavier one and repeat this operation until the first weight is found that is too heavy. Replace this weight by the next lighter weight and this will be the first weight to be retained on the balance pan. Continue adding the next consecutive lighter weight and test by releasing the beam support after each weight addition. When the weights smaller than 1 gram are used, release the beam support and use the pan rests. Continue adding weights and testing until within the range covered by the rider. Close the balance case door and complete the weighing with the rider.

Do not touch objects to be weighed, the balance or weights with the hands. Handle the weights with the weight forceps and carefully return them to their proper places in the box. Place the fractional weights right side up with the bent corner at the right. Always count the weights twice and notice if they check with those missing from the box. Before leaving the balance have all weights returned to the box, the rider removed from the beam, the beam and pans lifted off their knife-edge supports, the pan rests raised and the pans and balance floor clean.

Glassware, its use and care

Volumetric glassware, in particular, should be kept clean and free-draining. If the glassware does not drain free and dry (no drops of water adhering to the glass) it should be cleaned with cleaning solution and rinsed several times with distilled water.

The standard procedure for delivering the calibrated volume from a pipette is as follows: (1) after filling to the mark allow the pipette to drain normally (do not blow into it). (2) hold it above the liquid for fifteen seconds to allow it to drain. (3) touch the tip of the pipette to the surface of the liquid making no further attempt to remove the solution which remains in the tip.

All glassware should be cleaned with cleaning solution or powders, rinsed thoroughly with distilled water and allowed to drain dry. Hydrochloric (muriatic acid) is often more effective in cleaning than cleaning solution. This is particularly the case where the deposits (iron and carbonates) from hard water occur. Cleaning should be done as soon as possible after use so that the apparatus is always dry and ready for use.

Care and use of platinum

Platinum dishes are very desirable for solids and loss on ignition determinations. Platinum fuses at 1770°C . but does not soften to any extent at the

temperatures used for ignition. It resists the action of all single acids if pure. It is dissolved by chlorine solutions and, therefore, by aqua regia. Hydrochloric acid often contains traces of free chlorine which will attack the platinum.

Platinum alloys with most metals, especially those in compounds which are easily reduced. When heated for a long time in contact with carbon it becomes brittle, forming carbide of platinum. This is noticed when a dish is heated in the reducing flame of a burner. For this reason the tip of the inner cone of a burner flame should always be below (not against) the bottom of a platinum dish.

The following precautions should be observed when using platinum:

- (1) Do not heat with compounds of lead, tin, zinc, alkali hydroxides and other compounds of metals which are easily reduced.
- (2) When igniting with a burner keep the inner cone of the flame below the bottom of the dish. (Avoid use of the yellow flame.)
- (3) Handle carefully and avoid bending. Use platinum tipped tongs.
- (4) For cleaning use a solvent suitable for the material to be removed. Cleaning solution should be used for organic matter, hydrochloric acid for insoluble carbonates or metallic oxides, fusion with sodium carbonate for silica, and fusion with potassium bisulphate for such metallic compounds as will not be removed by acids.
- (5) Dull surfaces should be polished lightly with wet emery, slime or round sand. Do not scrape with files or glass rods.

Formation and Treatment of Precipitates

Gravimetric determinations in most cases depend upon the precipitation of a very slightly soluble

compound, filtering the same, freeing the precipitate of soluble compounds and drying or igniting, and weighing. Certain precautions must be exercised in these procedures. One of the first is the formation of a precipitate of sufficiently large particles so as to be retained on the filter paper. Heating, applying the precipitating reagent slowly and constant stirring are all factors in the production of large particles. The application of the precipitating agent slowly produces a small number of particles upon which the remaining precipitate grows. Heating and stirring tends to redissolve the smaller particles and reprecipitate them on the larger ones resulting in the formation of larger particles.

If the precipitate is to be ignited and weighed it must be filtered onto quantitative filter paper, that is, paper having a low ash content. The weight of ash in a 9 cm. quantitative filter paper should not be greater than 0.00005 to 0.0001 grams.

Before a precipitate is weighed it must be washed free from the soluble impurities. The first washings may be made in the precipitation vessel by decantation. To accomplish this, the major portion of the precipitate is allowed to settle and the supernatent solution decanted through the filter paper. A small portion of wash water is added and thoroughly mixed with the precipitate and this decanted through the paper. After several washings of this kind the precipitate is entirely transferred to the paper and again washed with several small portions of wash water. Many small portions of wash water are much more effective in washing than a few larger portions for the same total volume used.

After the precipitate is filtered and washed, the paper must be folded, placed in the crucible and dried before ignition. Usually the ignition, in event no muffle furnace is available, should be carried out in the oxidizing flame of a burner of the Meeker type. The oxidizing flame is that portion outside of the inner cone of the flame. The inner

cone of a gas flame is a reducing flame. If a burner is used for ignition, the paper must be completely burned in a low flame. The flame is increased and the crucible inclined on its side to facilitate the ignition of the carbon of the paper. The flame is then further increased until the desired temperature of ignition is obtained.

Records

All data, including weighings, calculations and details of computations, should be recorded in some form of bound notebook. This permits a ready reference to all previous records and makes all laboratory data available at any time for checking of calculations and results.

Considerable time can be saved in routine analysis if these notebooks are made up locally and patterned after a form to comply with the specific needs of the laboratory. All data should be entered on the right-hand pages of the book, reserving the left-hand page for calculations.

The two forms which follow, one for a water and the other for sewage plant laboratory, are considered typical and are offered as a basis for the development of forms for laboratory records. Most plants develop record forms in which all of the laboratory data as well as other plant data is compiled. This data may be in the form of a weekly, monthly or yearly record. These forms, also, must be made to fill the specific needs.

Water Filtration Plant

Form for Laboratory Data

Date	Analyst	
Sample	Raw	Treated
Temperature		
Color		
Odor		
Turbidity		
pH		
Alkalinity Burette reading after Burette reading before Ml. 0.02 N acid used P.p.m. alkalinity		
Free carbon dioxide Burette reading after Burette reading before Ml. of N/44 alkali used P.p.m. free CO ₂		
Total hardness, soda reagent Burette reading after Burette reading before Ml. of 0.02 N acid used P.p.m. total hardness		
Non-carbonate hardness, p.p.m.		
Residual chlorine, p.p.m.		
Total iron, p.p.m.		
Residual alum, p.p.m.		

Remarks:

Sewage Treatment Plant

Form for Routine Laboratory Data

Date

Analyst

Sample	Raw	Settled	Filtered	Final	Sludge
pH					
TOTAL SOLIDS					
Wt. of dish and solids					
Wt. of dish					
Wt. of solids					
p.p.m. total solids					
TOTAL LOSS ON IG- NITION					
Wt. of dish and solids					
Wt. after ignition					
Loss in weight					
p.p.m. loss on ignition					
SUSPENDED SOLIDS					Remarks
Wt. of xible and solids					
Wt. of xible					
Wt. of solids					
p.p.m. suspended solids					
SUSP. LOSS ON IG- NITION					
Wt. of xible and solids					
Wt. after ignition					
Loss in weight					
p.p.m. loss on ignition					
SETTLEABLE SOLIDS					
Ml. per liter					
5-day B.O.D.	Raw	Settled	Filtered	Final	
Incubation period, days	0	5	0	5	0
Per cent dilution					5
Burette reading, after					
Burette reading, before					
Ml. thiosulphate used					
P.p.m. dissolved oxygen					
P.p.m. B.O.D.					

Lists of Apparatus and Chemicals

For convenience in preparing these lists the laboratories have been classified according to the chemical determinations required for the control of the various types of treatment plants. These are basic lists to be used in outfitting the various laboratories and may require additions or deductions to suit the special situations. The classification has been made as follows:

- (A) Laboratories for the control of water plants with chlorine treatment only.
- (B) Laboratories for the control of water plants having coagulation, filtration and chlorination.
- (C) Laboratories for the control of water plants having softening, coagulation, filtration and chlorination.
- (D) Laboratories for sewage treatment plants in which settleable solids, relative stability, hydrogen ion (pH) and chlorine determination are made.
- (E) Laboratories for sewage treatment plants where solid tests, oxygen determinations, pH and chlorine tests are made.
- (F) Laboratories for sewage treatment plants in which all the usual control tests in this manual are made.

List of Apparatus

Name	Number of Pieces					
	A	B	C	D	E	F
Analytical balance		1	1		1	1
Balance weights		1	1		1	1
Trip scales		1	2		1	1
Scale weights		1	2		1	1
Drying oven			1		1	1
Muffle furnace			1		1	1
Incubator 20°C					1	1
Hydrogen ion apparatus	1		1	1	1	1
Nitrogen distillation apparatus						1
Gas analysis apparatus						1
Imhoff cones				3	3	4
Sampling can (D.O.)					1	1
Beakers, 2 liter	2		4			2
Beakers, 1 liter	4		6		2	2
Beakers, 600 ml.	4		6			2
Beakers, 400 ml.	2		4		6	6
Beakers, 250 ml.	6		12		6	6
Beakers, 50 ml.	3		4			2
Beaker covers, 75 mm.	6		12			6
Bottles, glass-stoppered, 32 oz.	6	24	36		6	24
Bottles, glass-stoppered, 16 oz.	4	8	12		3	12
Bottles, glass-stoppered, 8 oz.	8		12	12	24	72
Wash bottles, 1 liter	2	6	8		2	4
Burettes, 50 ml.		8	12		2	4
Burners, Meeker		2	2		2	2
Burners, Bunsen		2	6		2	6
Clamps, burette		6	6		2	4
Clamps, condenser						2
Clamps, holders						2
Clamps, pinch		12	12		4	6
Nessler tubes, 100 ml.	8	12	12	3	3	24
Condenser						1
Corks, bag	2	4	6		2	3
Cork borers		1	1		1	1
Crucibles, 46 mm.		4	12			6
Crucibles, Gooch, 25 ml.					4	18
Crucible, Gooch, holders						4
Graduated cylinders, 1 liter		2	4		2	2
Graduated cylinders, 100 ml.		2	6		2	2
Graduated cylinders, 25 ml.		2	4		1	2
Graduated cylinders, 10 ml.		2	4		1	2
Desiccators, 250 mm.		1	3		1	2
Evaporating dishes, 75 mm.		6	12		4	12
Evaporating dishes, 90 mm.		4	6		2	2

	A	B	C	D	E	F
Files		2	2		1	2
Filter paper, 9 cm., packages		6	12			6
Filter paper, 12 cm., packages		1	2			
Filter paper, quantitative, 9 cm.			2			1
Erlenmeyer flasks, 500 ml.		6	8			
Erlenmeyer flasks, 250 ml.		12	24		4	12
Volumetric flasks, 1 liter		4	6		2	3
Volumetric flasks, 500 ml.			2			2
Volumetric flasks, 250 ml.		4	6			4
Volumetric flasks, 200 ml.		6	12			
Volumetric flasks, 100 ml.		2	4		2	2
Funnels, 65 mm.		6	12			6
Funnels, 90 mm.		2	2			
Funnels, Buechner, 80 mm.						1
Glass Tubing, 7 mm., lbs.		5	10		1	3
Kjeldahl flasks, 500 ml.						4
Kjeldahl flasks, bulbs						4
Pipettes, 100 ml.		4	6		2	2
Pipettes, 50 ml.		4	6			2
Pipettes, 25 ml.		4	6			2
Pipettes, 10 ml.		4	6			2
Pipettes, 5 ml.						2
Pipettes, 1 ml.	4	6	12	2	5	12
Pipettes, graduated 1/100, 1 ml.					2	6
Pipettes, graduated 1/10, 10 ml.		2	6		2	6
Pipettes, graduated 1/10, 5 ml.			6			
Rings, iron, 4 inch		2	4		2	6
Rings, iron, 3 inch		2	6			
Spatulas, 3 inch					2	3
Iron supports		3	6		1	6
Test tubes, assorted		24	36		36	72
Thermometers, -10 to 110°C		2	4		2	2
Thermometers, 0 to 250°C						2
Crucible tongs		4	6		2	4
Triangles, 2 inch		6	6		2	4
Wire gauze, 4 inch		6	6			4
Suction flasks, 500 ml.					2	4
Rubber tubing, 1/4 inch, (ft.)		30	50		24	48
Rubber stoppers, assorted, (lbs.)		5	10		1	2
Desiccator plates, 230 mm.		1	3		1	2
Water suction pumps					2	4
Glass rods, 6 mm., (lbs.)		1	2		1	1
Soxhlett flask, 150 ml.					2	2
Tripods		2	2		1	4
Evaporating dish, platinum		2	2			
Water bath, 6 openings		1	1		1	
Platinum tipped tongs		1	1			

	A	B	C	D	E	F
Crucible tongs, 18 inch handle			1		1	1
Dropping bottles, 60 ml.		3	6		4	6
Burette support	1		2		1	2
Funnel support	1		1		1	1
Test tube support	1		1		1	1
Test tube brush	2		3		3	3
Jar brush	1		2		2	
Turbidimeter, Jackson	1		1			
Mortar and pestle	1		1			

List of Chemicals

Name	Quantity (pounds)					
	A	B	C	D	E	F
Sulphuric acid, C.P.		18	27	9	9	18
Sulphuric acid, Tech.		9	18	9	9	18
Potassium dichromate, Tech.		5	10		5	5
Sodium carbonate, anhydrous	1/2		1			1
Phenolphthalein (gms.)		25	50			25
Methyl orange (gms.)		25	50			25
Sodium hydroxide, sticks		5	10		5	5
Hydrochloric acid, C.P.		6	12			12
Sodium thiosulphate crystals	1/2		1		1	1
Ammonium carbonate	1/2		1/2			
Chloroform	1/2		1/2		1/4	1/4
Potassium biniodate						
Potassium iodide		1	2		1	1
Starch, corn		1	1			
Potassium permanganate			1			1
Ammonium oxalate crystals			1			1/2
Asbestos fiber					1/4	1/4
Alcohol, grain (qt.)		1	1			
Castile soap powder		1	1			
Ammonium hydroxide		4	8			8
Calcium carbonate, C.P.	1/2		1			
Calcium hydroxide, C.P.			1			
Hydroxylamine hydrochloride	1/16		1/4			
Benzidine hydrochloride	1/16		1/4			
Potassium chromate, C.P.	1/4		1/4			1
Silver nitrate, C.P.	1/4		1/4			1/2
Sodium chloride, C.P.	1/2		1			1/2
Aluminum sulphate crystals	1		1			
Bromine			1/4			
Ammonium chloride			1			1
Disodium phosphate			1			
Barium chloride			1			
Barium hydroxide			1			
Platinic chloride						
Potassium chloroplatinate (gms.)		1	1			
Cobaltous chloride	1/4		1/4			
Ferrous ammonium sulphate	1/2		1/2			
Potassium thiocyanate	1/2		1/2			
Potassium ferricyanide						
Manganous sulphate crystals			1		5	5
Nitric acid, C.P.						7
Phosphoric acid						
Alizarine Red S. (gms.)	10		10			
Sodium bicarbonate		1	1		1	1

	A	B	C	D	E	F
Acetic acid, glacial						
Fuller's earth		1	1			
Mercuric chloride						1
Potassium hydroxide						2
Mono-potassium phosphate						
Di-potassium phosphate						
Silver nitrite (oz.)						1
Sulphanilic acid						
A-naphthylamine hydrochloride					1	
Glass wool						
Silver sulphate						
Phenol						
Sulphuric acid, fuming						
Potassium nitrate						1
Potassium oxalate						1
c-tolidine (gms.)	25	25	25	25	25	25
Copper sulphate						1
Potassium dichromate, C.P.						
Iodine						1/4
Methylene blue (gms.)				10	10	10
Sodium hypochlorite (oz.)	4	4	4			
Molybdic acid						1
Salicylic acid						1/2
Boric acid						1
Phenolphthalin						
Thymolphthalein						
Potassium chloride						1
2, 6-dibromoquinonechloroimide						
Potassium bromate						
Potassium bromide						
Hydroquinone						1
Ferric ammonium sulphate						1
Litmus paper (vials)	2		4			4
Potassium sulphate crystals						1

Atomic Weights

Element	Symbol	Atomic Weight
Aluminum	Al	26.97
Barium	Ba	137.36
Bromine	Br	79.92
Calcium	Ca	40.08
Carbon	C	12.00
Chlorine	Cl	35.457
Chromium	Cr	52.00
Copper	Cu	63.57
Hydrogen	H	1.008
Iodine	I	126.932
Iron	Fe	55.84
Magnesium	Mg	24.32
Manganese	Mn	54.93
Molybdenum	Mo	96.00
Nitrogen	N	14.008
Oxygen	O	16.00
Phosphorus	P	31.02
Platinum	Pt	195.23
Potassium	K	39.10
Silicon	Si	28.06
Silver	Ag	107.88
Sodium	Na	22.997
Sulphur	S	32.06

Molecular and Equivalent Weights

Compound	Formula	Molecular Weight	Equivalent Weight
Aluminum sulphate	$\text{Al}_2(\text{SO}_4)_3$	342.14	57.02
Alum, crystals	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	666.43	111.07
Aluminum oxide	Al_2O_3	101.94	16.99
Ammonia	NH_3	17.03	17.03
Ammonium chloride	NH_4Cl	53.50	53.50
Ammonium hydroxide	NH_4OH	35.05	35.05
Ammonium nitrate	NH_4NO_3	80.05	80.05
Ammonium oxalate	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	124.08	62.04
Ammonium oxalate, crystals	$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	142.09	71.05
Barium chloride, crystals	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	244.31	122.15
Barium sulphate	BaSO_4	233.42	116.71
Boric acid	H_3BO_3	62.02	
Calcium carbonate	CaCO_3	100.08	50.04
Calcium chloride	CaCl_2	110.99	55.50
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	74.10	37.05
Calcium oxalate	CaC_2O_4	128.08	64.04
Calcium oxide	CaO	56.08	28.04
Calcium sulphate	CaSO_4	136.14	68.07
Carbon dioxide	CO_2	44.00	
Copper sulphate	CuSO_4	159.66	79.83
Ferrous ammonium sulphate	$\text{FeSO}_4 (\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$	392.13	196.07
Ferrous sulphate	FeSO_4	151.90	75.95
Ferrous sulphate, crystals	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.01	139.00
Ferric chloride	FeCl_3	162.21	54.07
Ferric chloride, crystals	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	270.30	90.10
Ferric hydroxide	$\text{Fe}(\text{OH})_3$	106.86	35.62
Ferric oxide	Fe_2O_3	159.68	26.61
Ferric sulphate, crystals	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	562.00	93.67
Ferric sulphocyanate	$\text{Fe}(\text{CNS})_3$	230.04	76.68
Hydrochloric acid	HCl	36.47	36.47
Hydrogen sulphide	H_2S	34.08	17.04
Magnesium ammonium phosphate	MgNH_4PO_4	137.38	
Magnesium carbonate	MgCO_3	84.32	42.16
Magnesium bicar- bonate	$\text{Mg}(\text{HCO}_3)_2$	146.34	73.17
Magnesium chloride	MgCl_2	95.23	47.62
Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	58.34	29.17

Compound	Formula	Molecular Weight	Equivalent Weight
Magnesium pyrophosphate	$Mg_2P_2O_7$	222.68	
Magnesium sulphate	$MgSO_4$	120.36	60.18
Magnesium sulphate, crystals	$MgSO_4 \cdot 7H_2O$	246.50	123.24
Manganous sulphate	$MnSO_4$	150.99	75.50
Manganous sulphate, crystals	$MnSO_4 \cdot 4H_2O$	223.05	111.53
Molybdic acid	H_2MoO_4	162.02	
Nitric acid	HNO_3	63.02	63.02
Oxalic acid	$H_2C_2O_4$	90.02	45.01
Oxalic acid, crystals	$H_2C_2O_4 \cdot 2H_2O$	126.05	63.02
Phosphoric acid	H_3PO_4	98.04	32.68
Phosphorous pentoxide	P_2O_5	142.05	
Platinic chloride	$PtCl_4$	337.06	84.76
Potassium chloride	KCl	74.56	74.56
Potassium chlorplatinate	K_2PtCl_6	486.17	
Potassium chromate	K_2CrO_4	194.20	
Potassium thiocyanate	KCNS	97.17	97.17
Potassium cyanide	KCN	65.11	65.11
Potassium dichromate	$K_2Cr_2O_7$	294.20	98.07°
Potassium ferricyanide	$K_3Fe(CN)_6$	329.19	
Potassium hydroxide	KOH	56.11	56.11
Potassium iodide	KI	166.03	166.03
Potassium permanganate	KMnO ₄	158.03	31.61°
Potassium nitrate	KNO ₃	101.11	101.11
Potassium oxalate, crystals	$K_2C_2O_4 \cdot H_2O$	184.22	92.11
Potassium sulphate	K_2SO_4	174.26	87.13
Silica	SiO_2	60.06	
Silver chloride	AgCl	143.34	143.34
Silver chromate	Ag_2CrO_4	331.76	
Silver nitrate	$AgNO_3$	169.89	169.89
Silver sulphate	Ag_2SO_4	311.82	155.91
Silver nitrite	$AgNO_2$	153.89	76.94
Sodium carbonate, anhydrous	Na_2CO_3	105.99	53.00
Sodium bicarbonate	$NaHCO_3$	84.00	84.00
Sodium chloride	NaCl	58.45	58.45
Sodium hydroxide	NaOH	40.00	40.00

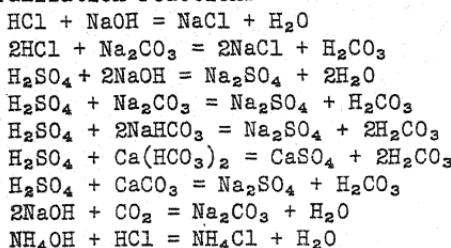
° In acid oxidation and reduction.

Compound	Formula	Molecular Weight	Equivalent Weight
Sodium hypochlorite	NaOCl	74.45	
Sodium sulphate	Na ₂ SO ₄	142.05	71.03
Sodium thiosulphate	Na ₂ S ₂ O ₃	158.11	158.11 ⁺
Sodium thiosulphate, crystals	Na ₂ S ₂ O ₃ · 5H ₂ O	248.19	248.19 ⁺
Sulphuric acid	H ₂ SO ₄	98.08	49.04
Water	H ₂ O	18.02	9.01

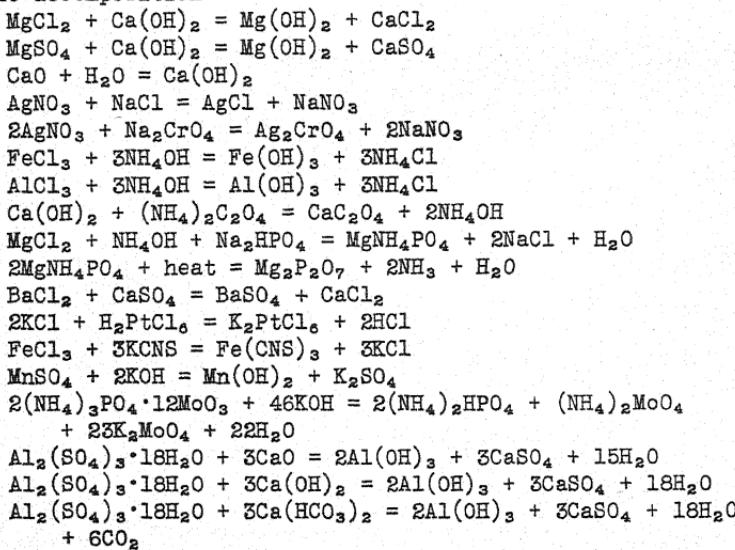
⁺ In oxidation-reduction reactions.

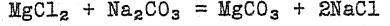
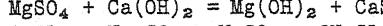
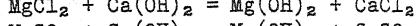
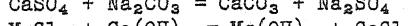
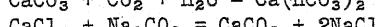
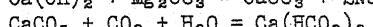
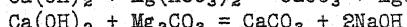
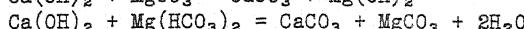
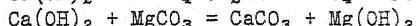
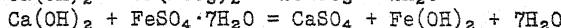
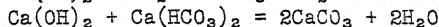
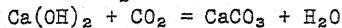
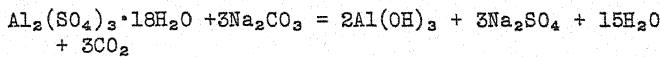
Chemical Equations

Neutralization reactions

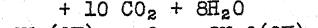
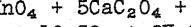
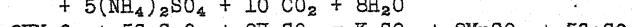
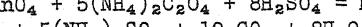
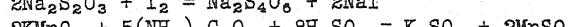
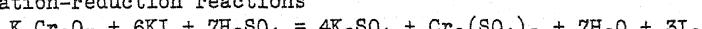


Double decomposition





Oxidation-reduction reactions



Conversion Factors

1 milligram per liter..... = 1 part per million

1 kilogram..... = 2.205 pounds

1 pound..... = 453.6 grams

1 grain per gallon..... = 17.12 parts per million

1 part per million..... = 0.0584 grains per gallon

1 gallon..... = 231 cubic inches

1 cubic foot..... = 7.48 gallons

1 cubic foot of water..... = 62.4 pounds

1 gallon of water..... = 8.34 pounds

1 gallon..... = 3.785 liters

1 liter..... = 0.2642 gallons

1 liter..... = 1.057 quarts

1 liter..... = 61.02 cubic inches

1 inch..... = 2.54 centimeters

1 centimeter..... = 0.3937 inches

1 cubic foot per second..... = 646,300 gallons per 24 hours

1 cubic foot per second..... = 449 gallons per minute

1,000,000 gallons per 24 hr. = 1.547 cubic feet per second

1,000,000 gallons per 24 hr. = 694 gallons per minute

1 part per million..... = 8.34 pounds per million gallons
1 pound per million gallons. = 0.1199 parts per million
1 acre..... = 43,560 square feet
1 gram..... = 15.432 grains
1 pound..... = 7000 grains
1 meter..... = 39.37 inches
1 cubic centimeter..... = 0.0610 cubic inches
1 cubic inch..... = 16.387 cubic centimeters
1 quart..... = 0.946 liters
1 gram..... = 0.0353 ounces
1 ounce..... = 28.3495 grams
Centigrade temperature = (Fahrenheit - 32) $\times \frac{9}{5}$
Fahrenheit temperature = (Centigrade $\times \frac{9}{5}$) + 32

Metric System of Measures and Weights

Length

1 meter..... = 10 decimeters (dm.)
1 decimeter..... = 10 centimeters (cm.)
1 centimeter..... = 10 millimeters (mm.)

Volume

1 liter (l)..... = 1000 milliliters (ml.)

Mass

1 kilogram (kg.)..... = 1000 grams (gm.)
1 gram..... = 1000 milligrams (mg.)

Chemical Factors

The following factors are derived from the equivalent weights of the various elements, radicals and compounds. To change from the weight of the known compound to its equivalent of the unknown multiply the weight of the known by the factor.

Known	Unknown	Factor
Al ₂ O ₃	Al	0.5303
Al ₂ O ₃	Al ₂ (SO ₄) ₃ ·18H ₂ O	6.5375
Al	Al ₂ O ₃	1.8856
Al ₂ (SO ₄) ₃ ·18H ₂ O	Al ₂ O ₃	0.1530
Al ₂ (SO ₄) ₃ ·18H ₂ O	CaO	0.2525
Al ₂ (SO ₄) ₃ ·18H ₂ O	Ca(OH) ₂	0.3325
Al ₂ (SO ₄) ₃ ·18H ₂ O	Na ₂ CO ₃	0.4776
BaSO ₄	SO ₄	0.4115
Ca	CaO	1.3390
Ca	CaCO ₃	2.4967
Ca	Ca(OH) ₂	1.8487
Ca	Ca(HCO ₃) ₂	4.0443
Ca	CaCl ₂	2.7693
Ca	CaSO ₄	3.3967
CaO	Ca	0.7149
CaO	Ca(OH) ₂	1.3208
Ca(OH) ₂	CaO	0.7571
CaO	CaCO ₃	1.7843
CaO	CO ₂	0.7846
CaCO ₃	Ca(OH) ₂	0.7404
CaCO ₃	CaO	0.5604
CaCO ₃	Mg	0.2430
CaCO ₃	CO ₂	0.4395
CaCO ₃	H ₂ SO ₄	0.9796
Ca(OH) ₂	CO ₂	0.5938
CO ₂	CaO	1.2750
CO ₂	Ca(OH) ₂	1.6840
CO ₂	CaCO ₃	2.2750
CO ₂	NaOH	1.8204
Fe	Fe ₂ O ₃	2.8483
Fe	FeCl ₃	2.9025
Fe	FeSO ₄ ·7H ₂ O	4.9787
Fe	FeSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	7.0224
Fe	CaCO ₃	1.7941
Fe ₂ O ₃	Fe	0.6994
Fe ₂ O ₃	FeCl ₃	2.0317
Fe ₂ O ₃	FeSO ₄	1.9026
FeSO ₄ ·7H ₂ O	FeSO ₄	0.5464
FeSO ₄ ·7H ₂ O	Fe	0.2008
FeSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	Fe	0.1424

Known	Unknown	Factor
Mg	CaCO ₃	4.1151
Mg	Mg(OH) ₂	2.3960
Mg	CaO	2.3059
Mg	Ca(OH) ₂	3.0467
Mg ₂ P ₂ O ₇	Mg	0.2184
Mg	MgSO ₄	4.9490
Mg	MgCl ₂	3.9105
Na	NaCl	2.5417
NaCl	Na	0.3934
Na ₂ CO ₃	Al ₂ (SO ₄) ₃ ·18H ₂ O	2.0959
Na ₂ CO ₃	CaCO ₃	0.9442
CaCO ₃	Na ₂ CO ₃	1.0591
H ₂ SO ₄	CaCO ₃	1.0208
H ₂ SO ₄	CaO	0.5720
H ₂ SO ₄	Ca(OH) ₂	0.7556
H ₂ SO ₄	Na ₂ CO ₃	1.0809
HCl	Na ₂ CO ₃	1.4534
NaOH	H ₂ SO ₄	1.2242
H ₂ SO ₄	NaOH	0.8168
NaOH	CO ₂	0.5493
H ₂ SO ₄	Mg	0.2480
AgNO ₃	Cl	0.2087
KMnO ₄	Ca	0.6341
KMnO ₄	O	0.2531
O	KMnO ₄	3.9507
Ca	KMnO ₄	1.5771
(NH ₄) ₂ C ₂ O ₄ ·H ₂ O	KMnO ₄	0.4448
K ₂ PtCl ₆	K	0.1608
K ₂ PtCl ₆	KCl	0.3067
K ₂ PtCl ₆	K ₂ O	0.1937
KMnO ₄	Mn	0.3476
N	NH ₄ Cl	3.8190
N	NH ₃	1.2158
NH ₃	N	0.8225
N	NO ₂	3.2844
NO ₂	N	0.3045
N	NO ₃	4.4266
NO ₃	N	0.2259
O	I	15.8665
I	O	0.0630
Na ₂ S ₂ O ₃ ·5H ₂ O	I	0.5114
Na ₂ S ₂ O ₃ ·5H ₂ O	O	0.003223
Na ₂ S ₂ O ₃ ·5H ₂ O	K ₂ Cr ₂ O ₇	0.3951
Na ₂ S ₂ O ₃ ·5H ₂ O	KIO ₃ ·HIO ₃	0.1309
I	Na ₂ S ₂ O ₃ ·5H ₂ O	1.9553
O	Na ₂ S ₂ O ₃ ·5H ₂ O	31.0238
K ₂ Cr ₂ O ₇	Na ₂ S ₂ O ₃ ·5H ₂ O	2.5307
KIO ₃ ·HIO ₃	Na ₂ S ₂ O ₃ ·5H ₂ O	7.6371

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